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"Atmospheric Processes in Plumes of Biomass Fires"
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Atmospheric Processes in Plumes of Biomass Fires (INT-95084-RJVA)

Final Report

To
USDA Forest Service
Rocky Mountain Research Station
Fire Sciences Laboratory
Missoula, Montana 59807

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Executive Summary

Samples analyzed are from fires in diverse regions (Zambia, southeast U.S., and Alaska) and vegetation types (Miombo, Dambo, mixed forest and gallberry, and boreal forest) and from ground samples and aircraft samples.

The samples were collected in canisters on the fields and analyzed in the laboratory at the Fires Sciences Laboratory in Missoula, Montana.

A method for trapping, concentrating, and measuring the halogenated hydrocarbon content of biomass burning emissions by gas chromatography was refined and utilized. Thirteen halocarbon gases were identified and quantified from the canister samples collected.

The CFC's were measured at high relatively constant concentrations for all samples, including background samples, but were all similar and showed no linear relationship with carbon monoxide (CO), a frequently measured gas that is a product of smoldering combustion. This indicates that these compounds are not important components of biomass burning emissions.

Six halogenated hydrocarbon compounds were found to have significant linear regression relationships with CO, at varying degrees for the fires sampled at the different sites. Of these the most important was methyl chloride, which was highly correlated with CO for most of the fires. Another compound which showed a strong linear relationship with CO for most of the fires was 1,1- dichloroethene.

Methyl bromide was found at high at significant levels for some fires, indicating levels in emissions may be dependent on vegetation content.

I. Introduction

Halocarbons have been considered the main sources of ozone depletion in the stratosphere. As late as 1950, photodecomposition of CH_3Cl provided about 85% of stratospheric chlorine, and only around the year 1970 did industrially produced organic chlorine compounds begin to overtake CH_3Cl as the major sources of stratospheric chlorine. In spite of the importance of CH_3Cl for the stratospheric ozone budget, its sources are not well defined and quantified. The ocean was considered to be the main source of halocarbons. Because plants contain chlorine in the form of electrolytes (i.e. dissolved salts), the emission of CH_3Cl from biomass burning has been measured since the 1970s.

A number of authors measure CH_3Cl in smoke from biomass fires, and estimate a source strength of 1.8Tg yr^{-1} (Andreae 1993), which account for one-half of the estimated global emission of this trace gas to the atmosphere. A total source of 3.4Tg yr^{-1} can be derived from the mean atmospheric concentration of 600ppt and a lifetime of 1.6 years. A similar situation applies to CH_3Br. Today, CH_3Br still accounts for about one-half of the bromine flux into the stratosphere, and the pyrogenic emission of CH_3Br has been estimated at about one-third of its global source strength of 100Gg yr^{-1}. In spite of the lower emission flux and concentration, bromide compounds represent a significant sink for stratospheric ozone due to the higher efficiency (a factor 50 relative to $Cl^{\cdot}$) of the catalytic cycle involving bromine.

Andreae et al in SAFARI 92 found that CH_3Cl was emitted preferentially in the smoldering phase of fires. CO is also emitted predominantly during this stage. Close linear correlation between smoldering-derived gases and CO is often measured which allows accurate estimations of trace gas emissions from smoldering fires for which the CO emissions are known. The background concentrations of CH_3Cl were about 0.6-1.1 ppb and 100-300ppb for CO. Concentrations of CH_3Cl up to 26ppb CH_3Cl and concentrations of CO up to 25ppm were often measured in ground sample collected from biomass burning. A high degree of consistency was found among fires in a wide variety of fuel types. The CH_3Br and CH_3I concentrations in smoke samples were highly correlated with the corresponding CH_3Cl or CO concentrations. An annual emission of 420Gg of CH_3Cl from savanna fires or about 10-15% of the global CH_3Cl source was obtained (based on the emission ratio 0.95 10^{-3} mole CH_3Cl / mole CO, and 20 10^{-6} mole CH_3Cl /mole CO_2) . These emissions can be compared to total worldwide CH_3Cl emissions from biomass burning of 1100 or 1500 Gg yr^{-1}, corresponding to one third to one half of the total CH_3Cl source strength. About 7Gg yr^{-1} of CH_3Br from savanna fires and about 20Gg.yr^{-1} of CH_3Br were produced from all worldwide biomass burning, which corresponds to 20% of the total emission of CH_3Br. The contribution of biomass burning of CH_3I (<10Tg yr^{-1}) is insignificant compared to the oceanic source of about 300Tg yr^{-1} . A field study FOS/DECAFE of trace gas emissions from biomass burning in Equatorial Africa at Latmo Reserve, was conducted in 1991(Bonsang, Rudolph, Lacaux & al 1995): background concentration were about 10ppb of CH_3Cl and 100ppb of CO and concentrations up to 100ppb CH_3Cl and similar magnitude for C_2HCl_3, C_2Cl_4, $C_2F_3Cl_3$, CCl_4, CH_3CCl_3, $CH_22ClCHCl_3$ and around 110 ppm CO were measured for ground samples collected during savanna biomass burning. A CH_3Cl emission ratio of 4.3 10^{-5} mole CH_3Cl/ mole CO_2 and an average emission ratio of 10 10^{-7}mol/mol CO_2 for other

halocarbons like CH_2Cl_2, $CHCl_3$, CCl_4, CH_3CCl_3, C_2HCl_3, C_2Cl_4, F-113 were found. The emission ratios were obtained with a decreasing magnitude with increasing complexity of the compounds and number of halogen atoms. The Latmo savanna is burnt each year with a mean biomass burning efficiency of 80% and a mean CO/CO_2 emission ratio of 6.1% at ground level during flaming condition. With a CO/CO_2 emission ratio of 10% or more, used as a criteria of smoldering combustion, they have concluded that 70% of the Latmo Reserve fires represent flaming combustion and from the samples of smoldering combustion they find an emission ratio of 8.9 10^{-5} mole CH_3Cl/mol CO, about twice of their average value, this supports the assumption that CH_3Cl is predominantly a product of smoldering combustion.

Ozone depletion : Mechanism and observation over the last ten years:
It is now understood that the Antarctic ozone depletion is caused by catalytic chlorine chemistry in the lower stratosphere. Cold air present at high southern altitudes permits the formation and persistence of polar stratospheric clouds (PSCs). Heterogeneous chemistry (ice, liquid, gas) on the ice clouds, followed by the reaction with sunlight, converts the reservoir species of chlorine (HCl and $ClONO_2$) into very reactive radicals such as Cl and ClO (Yibo J. & Zurek 1996)
The systematic increases of atmospheric CF_2Cl_2 (CFC12) and $CFCl_3$(CFC11), have caused the chlorine content to rich about 2.5ppbv compared to the natural level of
The heterogeneous processes act on both chlorine and nitrogen chemistry of the Antarctic about 0.6ppbv (Salomon S. 1990).lower stratosphere and set the stage for enhancement in the abundance of ozone-damaging forms of atmospheric chlorine. The following catalytic cycles are believed to be responsible for the ozone loss (Anderson J.G, Toohey D.W 1991):

$2 \times (Cl + O_3 \longrightarrow ClO + O_2)$
$ClO + ClO + M \longrightarrow Cl_2O_2 + M$
$Cl_2O_2 + h\mu \longrightarrow Cl + ClO_2$
$ClO_2 + M \longrightarrow Cl + O_2 + M$
Net : $2\,O_3 + h\mu \longrightarrow 3O_2$

Reactions involving the coupling between chlorine and bromide also contribute to the ozone destruction rate, particularly through the reaction cycle (Weisenstain D.K & al 1992):

$Cl + O_3 \longrightarrow ClO + O_2$
$Br + O_3 \longrightarrow BrO + O_2$
$ClO + BrO \longrightarrow Br + ClO_2$
$ClO_2 + M \longrightarrow Cl + O_2 + M$
net : $2O_3 \longrightarrow 3O_2$

Both mechanisms require sunlight in the near-ultraviolet to visible part of the spectrum, because at night ClO recombines to form Cl_2O_2, which is not reactive with O_3. BrO reacts to form BrCl and $BrONO_2$. The loss of O_3 is greatest when the exposure to sunlight is longest, at low latitudes and late spring (Brune W.H, Anderson J.G, Toohey D.W 1991). When the ClO and BrO abundance exceed 1200pptv and 5 pptv, respectively, these mechanisms are sufficient to explain the observed rate of O_3 destruction , which approaches 2% a day of the initial O_3. However this rate of O_3 loss must be maintained for more than a month in the springtime sun to account for the observed cumulative loss. To maintain ClO and BrO concentrations, the affected air must have NOx concentrations less than 20 ppt . If NOx is present in the air parcel, then chlorine can be shifted from

reactive forms back into the reservoir forms, such as $ClONO_2$ and HCl. However at temperatures lower than 78°F, the chlorine reserve forms exposed to the Polar Stratospheric Clouds will be converted to Cl_2 and dissociate into chlorine atoms.
A detailed analysis of the impact of chlorine on ozone abundance must consider the distribution of chlorine as a function of latitude, altitude, and season. Ko & al (1992) showed that there are two maxima in total inorganic chlorine production: the reaction of halocarbon species with OH (in the equatorial troposphere), and at 20-25 km in the lower tropical stratosphere due to photodissociation. Tough tropospheric production of inorganic chloride is large, almost all odd chloride produced in this region is converted to HCl and removed by rain or washout, and also because O_3 loss is much smaller than O_3 production and export in this region. But they find that 1.1.1trichloroethane, carbontetrachloride and C.F.C11 have contribution in the lower stratosphere, because of the photolysis process.
The presence of chloride radicals, particularly of ClO, and its anti linear correlation with O_3 has been confirmed by in situ measurements from aircraft (Anderson & al 1989,1991) and by remote sensing from UARS (Upper Atmospheric Research Satellite). However the observed 30% to 60% decline in total column O_3 concentrations during the last decade is qualitatively but perhaps not quantitatively consistent with chemical forcing of the ozone hole solely by chlorine, but also by bromine and iodine. Bromine and iodine concentrations are lower than chlorine concentration but have a faster catalytic cycle. The understanding of these observations require a better quantitative knowledge of the different halocarbons budgets in the atmosphere (e.g. sources, sink, distribution).

This is an area of study in which field data are quite sparse. Halocarbons have been identified as significant agents of ozone depletion in the stratosphere, but all the sources are not well defined and quantified. Industrially produced organochlorine compounds and ocean sources cannot explain quantitatively the ozone depletion observed.

We carried out the analysis by gas chromatography of smoke samples collected in canisters by the Fire Sciences Laboratory during field work in Zambia (summer 1996), the southeastern United States in March and April 97, and field work of fire emission sampling in Alaska in June 97. By identifying and quantifying halogenated compounds emitted during the prescribed fires, we characterized which halogenated hydrocarbons are emitted by understudy vegetation burning.
We will determine, with particular emphasis, the quantities of the following halocarbons in samples collected from these fires: methyl chloride, methyl bromide, chloroethane, 1,1-dichloroethene, methylene-chloride, cis-1,2-dichloroethylene, 1,1,1-trichloroethane, chloroform, carbon-tetrachloride, 1,2-dichloropropane, and CFC12, CFC114, CFC11, CFC113.
The concentrations of halocarbons in the canisters were correlated with each other and with CO. The CO data and other trace gas concentrations are available from analyses of some canisters at the Fire Science Laboratory.

II. Sampling System

The Fire Atmosphere Sampling System (FASS) was used for collecting canister samples (Ward & al, Journal of Geophysical Research, May 30,1995). This consists of a sampling head mounted on a tower, and two boxes on the ground that contain pumps and sample canisters, buried below ground to minimize the effects from high heat intensity. The sampling system was controlled by a software program that iniates sampling when a set temperature or carbon dioxide threshold is reached. Ambient air or smoke was drawn from the top of a 5-10 meter tower through a ¼" Teflon line by a modified KNF pump with a flow rate of 1.8 L min^{-1}. It passed through two Nupro stainless steel filters before entering the pump. The sample air then was directed through a manifold which had 4 solenoid valves (Angar Scientific), one attached to each canister. The sample was pressurized into an 850 ml electro-polished stainless steel canister over the duration of the phase of combustion. The sampling time was 6 minutes during the flaming phase and 15 minutes during the smoldering phase for savanna fires. A canister of background was collected prior to the fire.
The aircraft canister sample system uses similar components to the FASS. A Metal Bellows pump draws sample through stainless steel tubing from a port in the front window of the plane. The sample passes through a stainless steel fritted filter and then through a Tylan flow controller and into the canister through a solenoid valve. The flow rate is approximately 20 liters/minute, fill time for a canister about 10 seconds.

III. Analytical Method

1.Gas Chromatography

Halogenated compounds are cryogenically trapped and analyzed by gas chromatography (Hewlett-Packard 5890 series II) using a modified E.P.A method TO-14.
The cryogenic system includes a 4'long x 1/16"o.d (0.03"i.d.) stainless steel coiled trap packed with glass beads (Supelco, 80/120 mesh), a Tylan FC-280S mass flow controller, a Setra digital pressure gauge (model 304-1) , a vacuum pump (Welch, model 8905), and a Valco 6-port valve in a heated enclosure.
The trap is submerged in liquid nitrogen in a dewar at -196 °C. To trap and concentrate the gases. The sample in 865 ml canister is drawn through the flow controller and the valve to the cold trap by an evacuated canister. The flow rate of the sample is controlled at 5 $ml.min^{-1}$. The volume of the sample collected is determined from the pressure increase in the evacuated canister. The volume of the sample trapped is 100 ml.
After preconcentration of the sample, the valve is switched from the trap mode to the desorption mode, and the liquid nitrogen dewar is replaced by boiling water bath on a heated plate. The N_2 carrier gas of the GC then passes through the valve and the trap and returns to the GC where the sample is focused at the head of the column at -80 °C.

A J&W scientific DBVRX column (60 m long x 0.25 mm i.d.) is used for chromatographic separation. This column at -80°C acts as a stationary phase for focusing the compounds at the head of the column. The flow rate of the carrier gas N_2 is 1.3 ml/min with a column head pressure at 23 psi.
The compounds are detected with an electron capture detector (E.C.D). The doping with O_2 of the makeup gas Ar/CH_4 permits a high sensitivity of the E.C.D for monohalocarbons but will affect the linearity of the detector. The anode gas must be at 30 psi with a flow rate of 60 ml/min, a higher flow will reduce the sensitivity of the detector.

Temperature programs:

-detector temperature: 350 °C

-injector temperature: 200 °C

-oven temperature: -initial temperature at -80 °C, held 10 min, then increased at a rate of 30 C/minute to 40 C, than increased at a rate of 0.5 C to 56 C, then increased at a rate of 30/minute to 200 C final temperature, for 20 minutes to the end of the run. The total run time is 70 minutes.

2. Calibration:

The retention times of 17 compounds were identified by using several sets of standards:

-standard A containing four chlorofluoro carbons of 100 ppb:
CFC11 ($CFCl_3$), CFC113 (CCl_2FCClF_2), CFC114 (CF_2ClF_2Cl), CFC12(CF_2Cl_2)

-standard B containing 12 chlorinated hydrocarbons of 100 ppb: methyl-chloride , vinylchloride, chloroethane, 1,1-dichloroethene, methylene-chloride,1,1-dichloroethane, cis-1,2-dichloroethene, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbontetrachloride, 1,2-dichloropropane,

-standard C containing a methyl-bromide standard of 700 ppb and diluted to 0.5 -20ppb.

The accuracy of the method is determined by the reproducibility of the retention times and the ratio of the peak area to the concentration for each compound (or response factor) from multiple runs of the standard at 100 ppb. The linearity of each compound is determined by calibrating the standards described in the range of 0.1 to 10 ppb concentrations. The dilution of the standard to obtain the concentration desired is made by mixing the standard with ultra high purity N_2 in various proportions. A canister is filled first with the standard at a set pressure, and then N_2 is injected into the canister to the desired pressure, to dilute the standard. Each compound is identified by retention time and the peak area at different concentrations is determined.

IV. Field Sites

1. Zambia:

During the summer of 1996, early dry season burning of the Dambo and Miombo savannas in Zambia was conducted. The Miombo is a pure grassland savanna whereas the Dambo is a mixed shrubland- grassland. Zambia is part of the Central African Plateau. Its altitude ranges from 1000 m to 2000 m above sea level (Cole 1986). The field site is located approximately 7.5 km southeast of Kaoma, Western Province, Zambia in Kaoma Local Forest No.310 (14°86' S, 24°82' E). The district average annual rainfall is 900-1000 mm occurring mostly during from late November to April. Daily average temperatures in July which is the middle of the dry season, are 17.5 -20 °C. The elevation is approximatively 1170 m. Despite the fact that the site is a Protected Forest maintained by the Department of Forestry, both ecosystems are heavily utilized by local agriculturists and villagers for charcoal manufacturing, fuelwood collection, thatch harvesting, honey production, grazing, and agriculture. Local agricultural crops near the study site include cassava, ground nuts, maize, and sweet potatoes. The sites burn every one to two years to facilitate agricultural production and livestock grazing.

2. Southeast United States:

In the spring of 1997 fires were set at military bases in the southeastern U.S. (Ft.Stewart, Georgia; Eglin AFB, Florida; and Camp LeJeune, North Carolina) for the purpose of vegetation management and fuel reduction. The emissions and plume were sampled from an aircraft sampling system. The vegetation types were a mixed pine-hardwood, and gallberry. The impact of these fires in the production of halogens-because of their proximity to the coast, the vegetation and the ambient air may have a high halogen content. This may result in a higher concentration of halogenated compounds in the smoke samples

3. Alaska:

The Alaska canister samples were from wildfires in spruce boreal forest burning in June of 1997 near Fairbanks and in central Alaska. The fires were large, greater than 50,000 acres. They were sampled by the aircraft sample system from a twin engine plane.

V.RESULTS

1. Zambia Fires

The results of the canister analysis for the Zambia fires is presented in Figures 1-5. For the Zambia canister samples thirteen halogenated compounds were measured: methyl chloride, methyl bromide, methylene chloride, 1,1-dichloroethene, c-1,2 dichloroethylene, 1,2- dichloroethane, chloroform, 1,1,1- trichloroethane, carbon tetrachloride, and four CFC11, CFC112, CFC113, and CFC114. Methyl chloride was measured in a range of 0- 30 ppb, methylene chloride 0-0.6 ppb. There were high CFC background concentrations, as well as in all the samples, probably from the Teflon tubing. As a result this data for these compounds showed little of interest. The concentrations of all halogenated compounds in smoldering samples were low and near background concentrations. This was most likely due to the way samples were taken by the FASS sampling system. The entire flaming front and mix of flaming and smoldering combustion emissions were collected in the flaming canisters. All the results presented are derived from the background concentrations and the flaming combustion. The four halocarbons that were measured with sufficient quantity and accuracy were regressed vs. CO, CH_4, and CO_2. The regressions with CO had the highest degree of correlation, so only those are presented. (Figures 1-4). CO is also the most important indicator of smoldering combustion, when most halocarbon emissions are produced.

Linear correlation with CO:

Different linear relationships between the halogenated compound concentrations and CO were found, depending of the compounds and the type of vegetation: Miombo and Dambo savannas:

-for methyl-chloride: a strong linear correlation (r^2= 0.70) for Miombo and Dambo data combined.

-for methylene-chloride: different slopes for the two vegetation types(Miombo and Dambo, both with r^2= 0.73.

-for cis-1,2-dichloroethylene: different slopes for each type of vegetation, with r^2= 0.79 for Miombo and 0.61 for Dambo,

-for 1,2-dichloroethane: a different linear relationship for each type of vegetation, with a linear correlation of r^2= 0.56 for Miombo and a linear correlation of r^2=0.77.

-for methyl-bromide, 1,1-dichloroethene, chloroform, 1,1,1-trichloroethane, carbon tetrachloride and with the CFCs, there are no apparent linear linear correlations. Because of the low and constant concentration of methyl-bromide and chloroform during the flaming stage (0.01-0.02 ppb), it can assumed that this is at the detection limit of the E.C.D . Because of the high sensitivity of the E.C.D to CFCs compounds (10 to 100 times higher than other halogenated compounds), peak tailing for each CFC interfered with other peaks such as methyl bromide, 1.1 dichloroethene.

Even though the response of the E.C.D for 1.1.1 trichloroethane is very sensitive , the concentrations are very low: mostly less than 0.40 ppb. This resulted in low correlation of the emissions of 1.1.1 trichloroethane with CO.

Figure 1. Zambia fires. Methyl chloride vs. CO

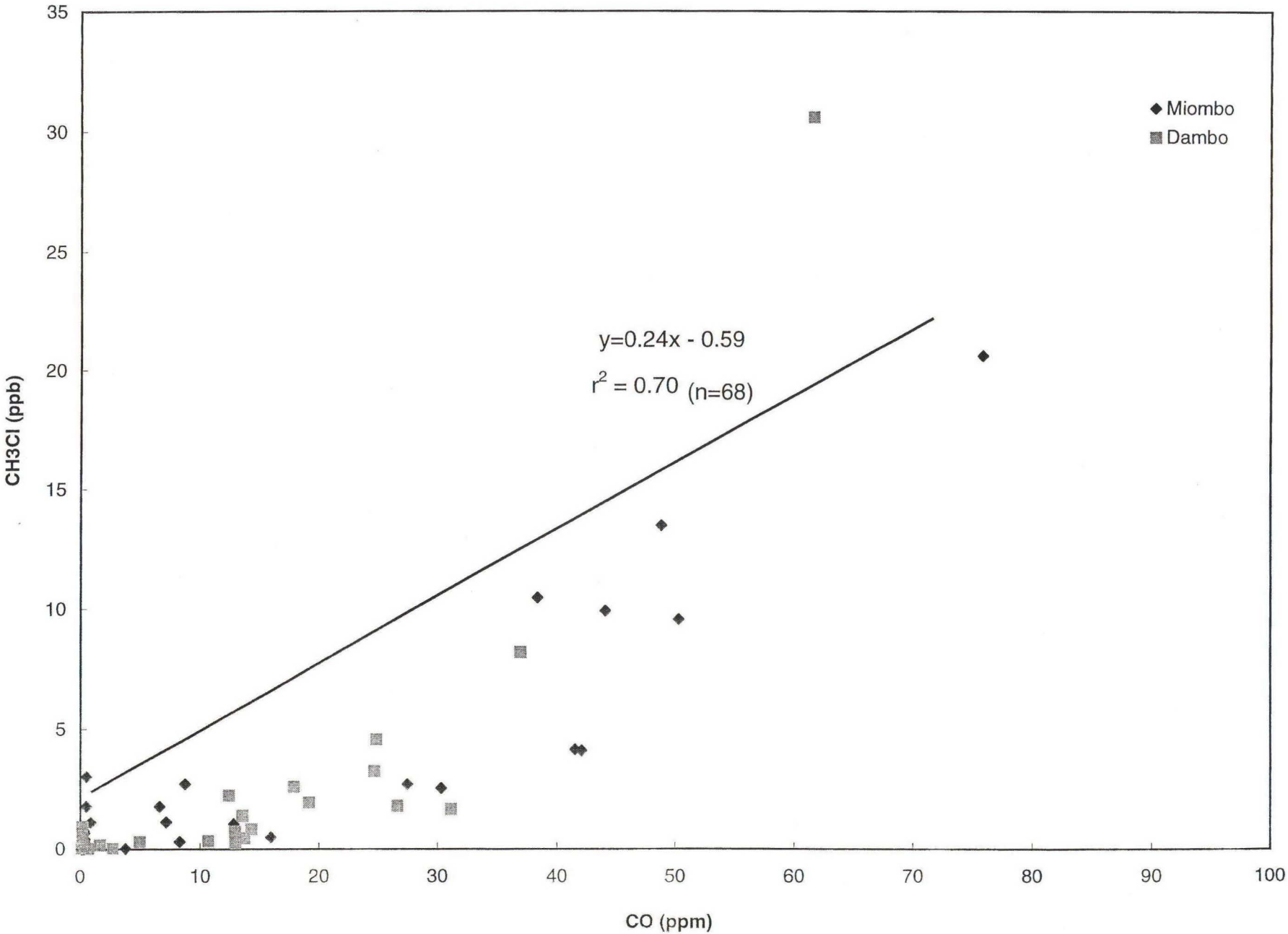


Figure 2. Zambia fires. 1,1-Dichloroethylene vs. CO

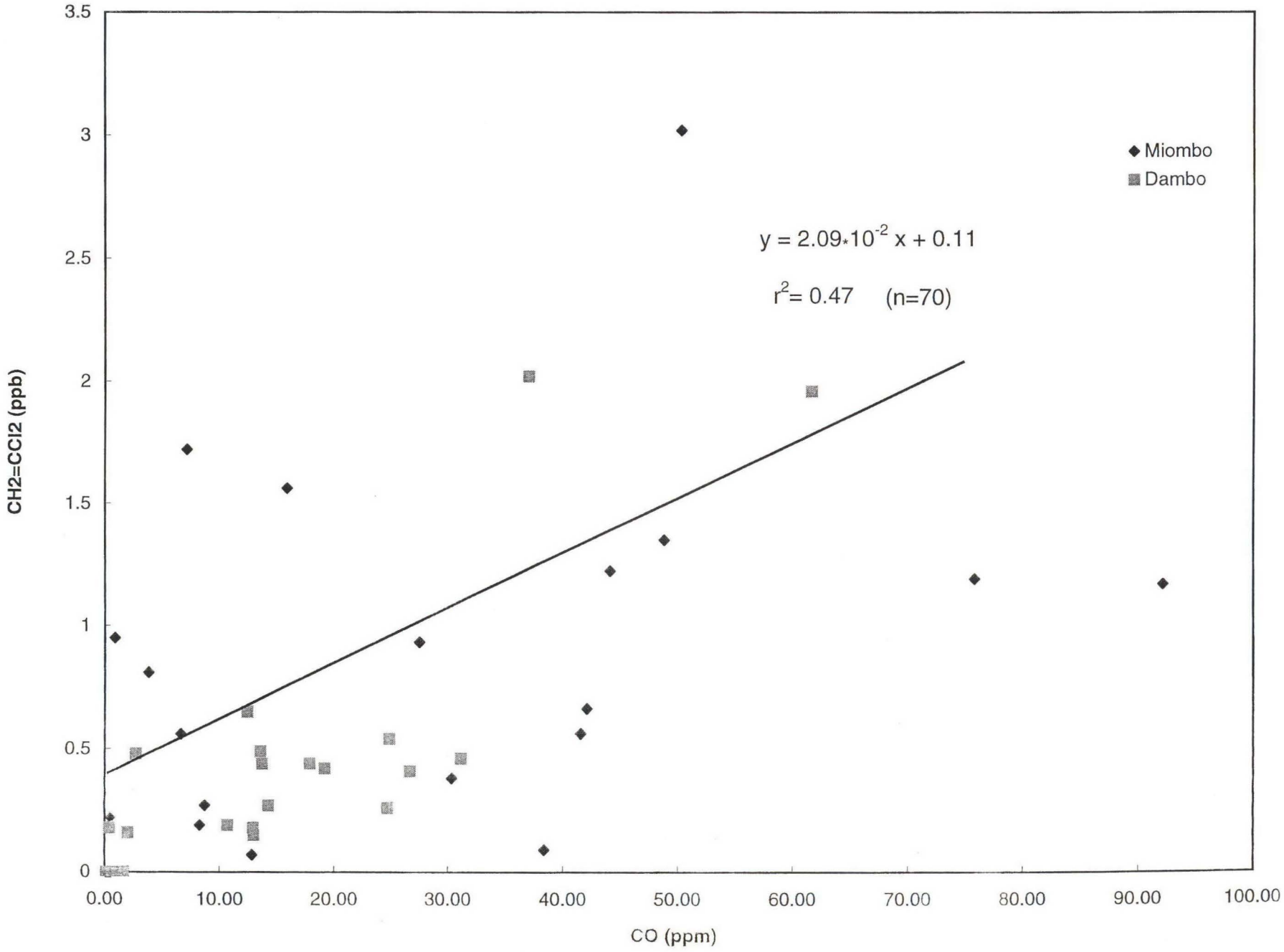


Figure 3. Zambia fires. Methylene chloride vs. CO

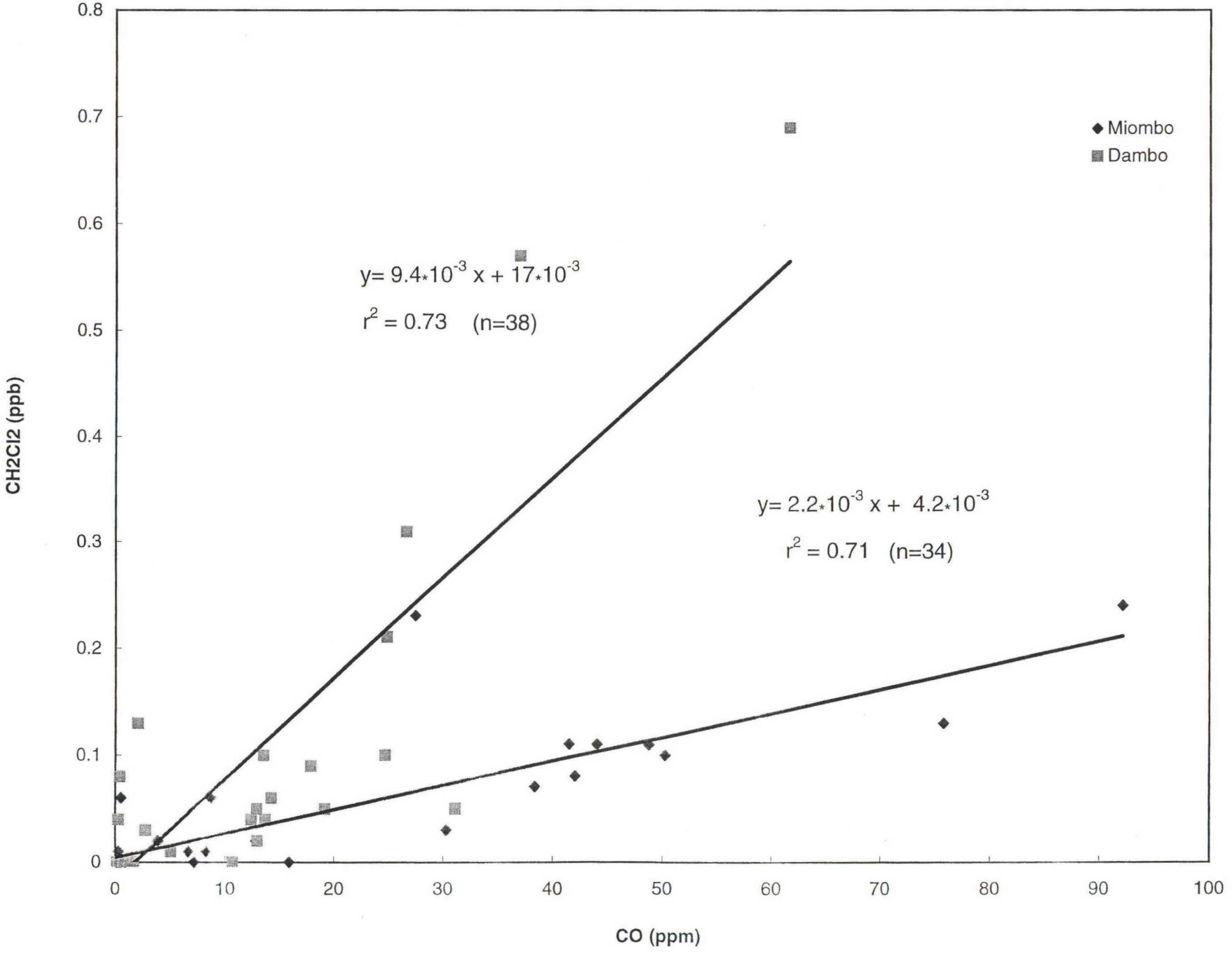
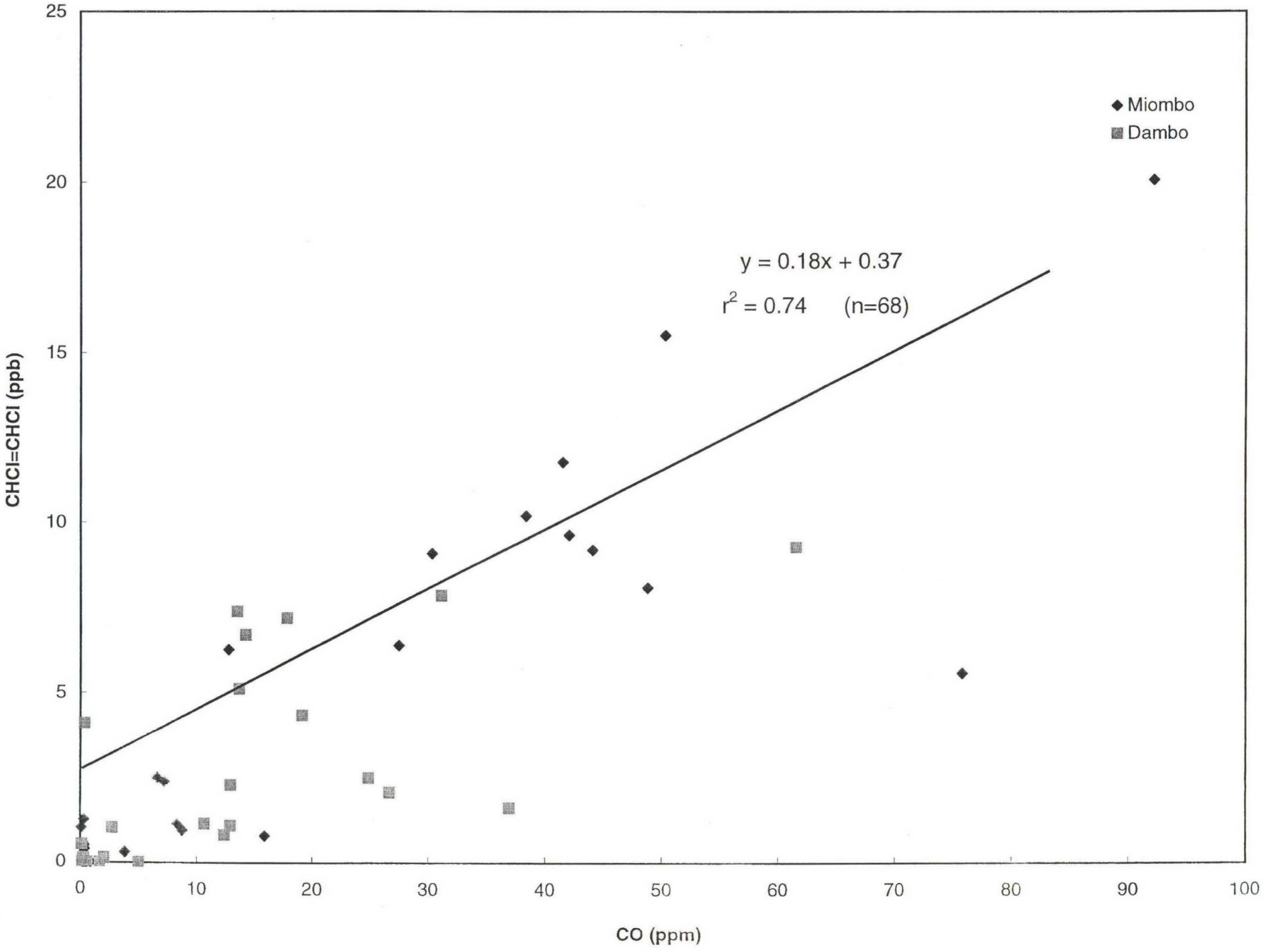


Figure 4. Zambia fires. cis-1,2-Dichloroethylene vs. CO



The concentration CFCs are constant at ambient level and indicate that fires are not a source of CFCs.
Based on the compounds that were detected and measured and had a significant linear relationship with CO the linear relationships between CO, emission factors as a ratio to CO were tabulated. These are useful in estimating the emissions of these compounds based on CO emissions.

Table 1. Emission factors for significant halogenated gases vs. CO (Zambia).

	ratio to CO		r^2	
	Miombo	Dambo	Miombo	Dambo
methyl-chloride	0.2454		0.71	
methylene-chloride	0.0023	0.0093	0.73	0.73
1,2-dichloroethane	0.0454	0.1017	0.56	0.77
cis-1,2-dichloroethylene	0.1941	0.1459	0.80	0.61

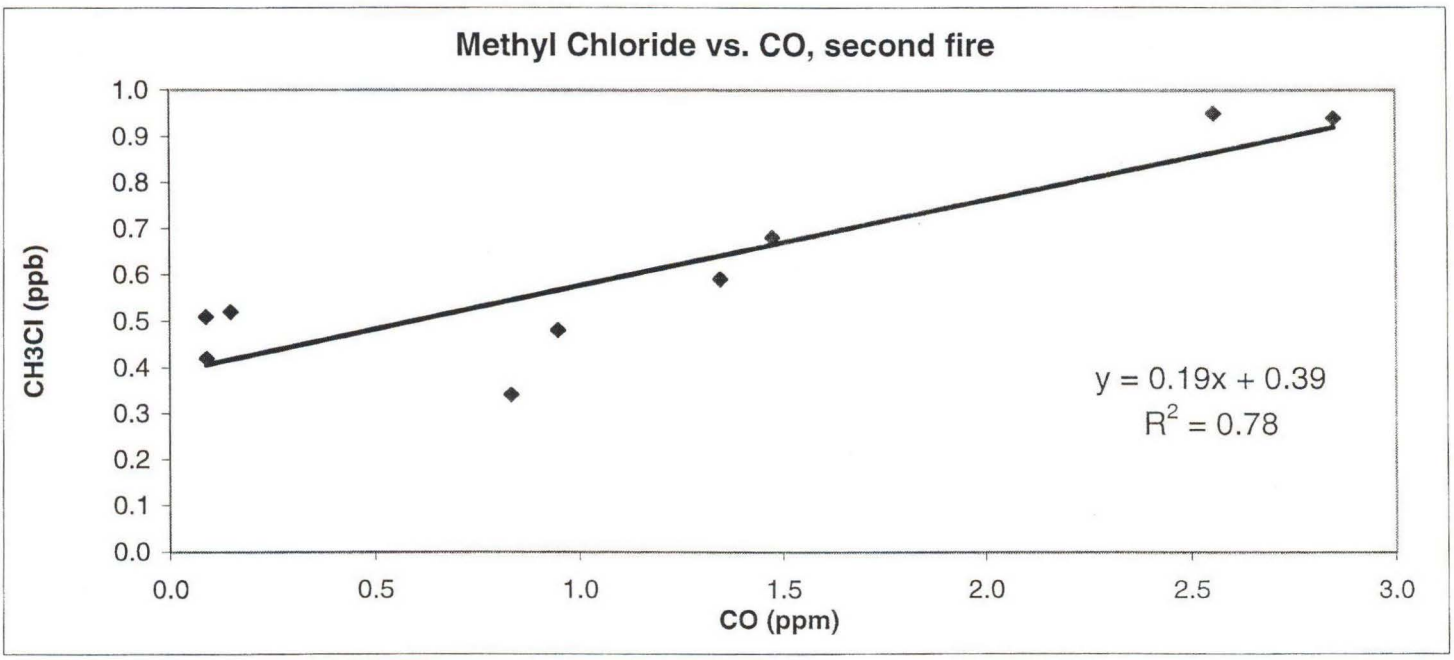
2. Southeast U.S. Fires:

There were 3 fires sampled at Ft. Eglin, 3 fires at Ft. Stewart, and 2 at Camp Lejeune. Each fire was sampled by aircraft, the principal sample scheme was to fly through the smoke plume to collect canisters. The concentrations of halocarbons in the aircraft samples are lower than the Zambia fires and representative of high altitude diluted concentrations. The samples were relatively free of background contamination and therefore the identification and quantification of halogenated compounds was very good. The concentrations range for the gases measured were:
350 to 600 ppm CO2
0 to 14 ppm CO
6 ppb to 0.01 ppb methyl chloride
12 to 0.01 ppb methyl bromide
10 to 0.01 ppb methylene chloride.
1 to 0.01 ppb other halocarbons.

Linear correlation with CO:

For the first Eglin fire, the concentrations of the aircraft canisters are constant and at background level. Therefore no correlation could be found. (CO<0.6ppm, CO2< 360ppm). The regressions for the other fires of halocarbons v. CO are presented in Figures 5-9. For all the Southeast sites we found two compounds having strong correlation with CO- methyl chloride and 1,1-dichloroethylene (Figures 5-13). This is due to relatively high concentrations of methyl chloride in the samples, as well as success in measurement by the gas chromatography method.

Figure 5: Eglin Fires, AirCraft Canisters



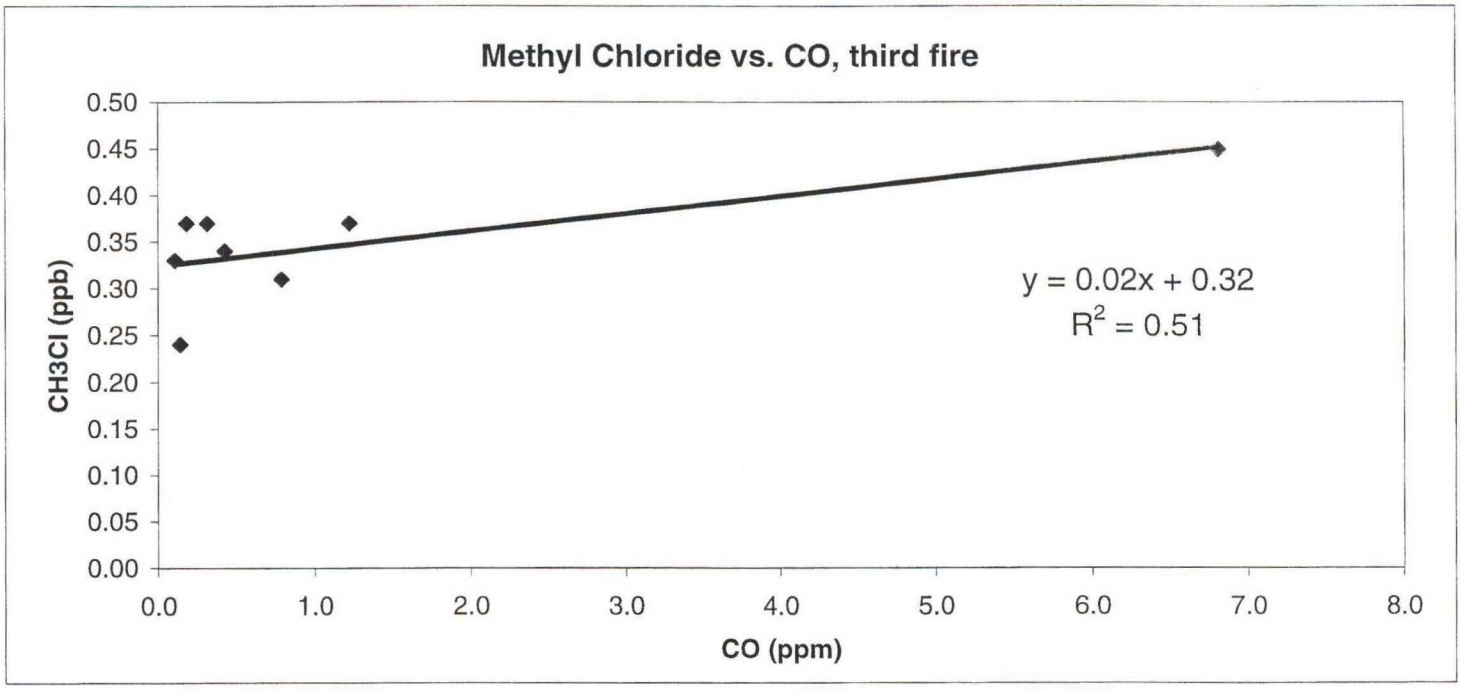
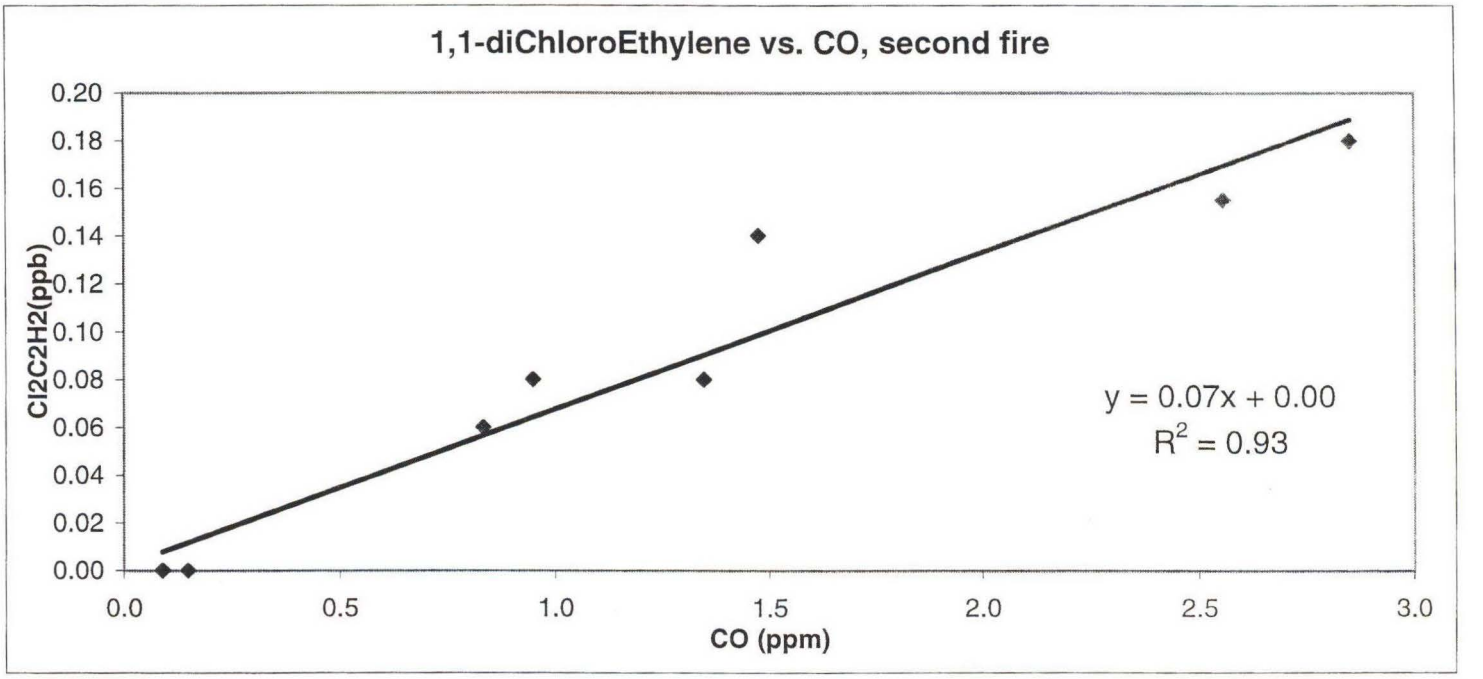


Figure 6: Eglin Fires, AirCraft Canisters



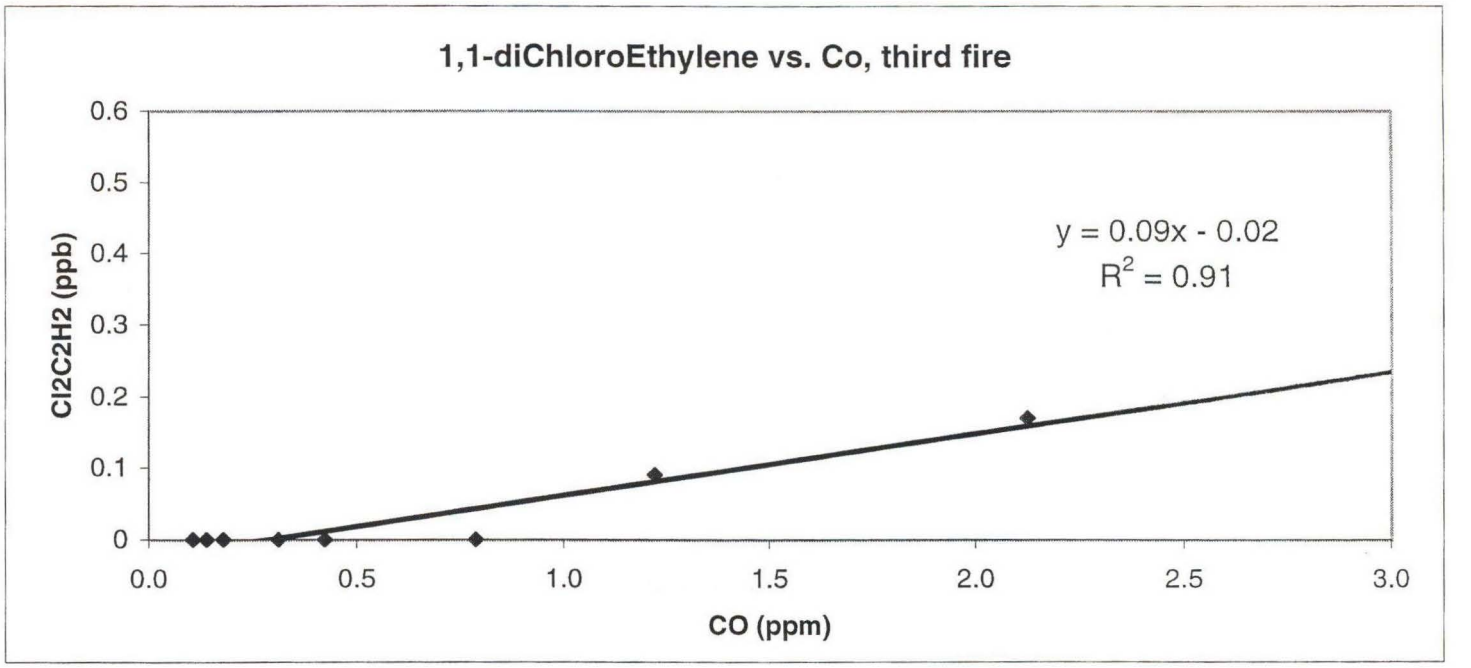
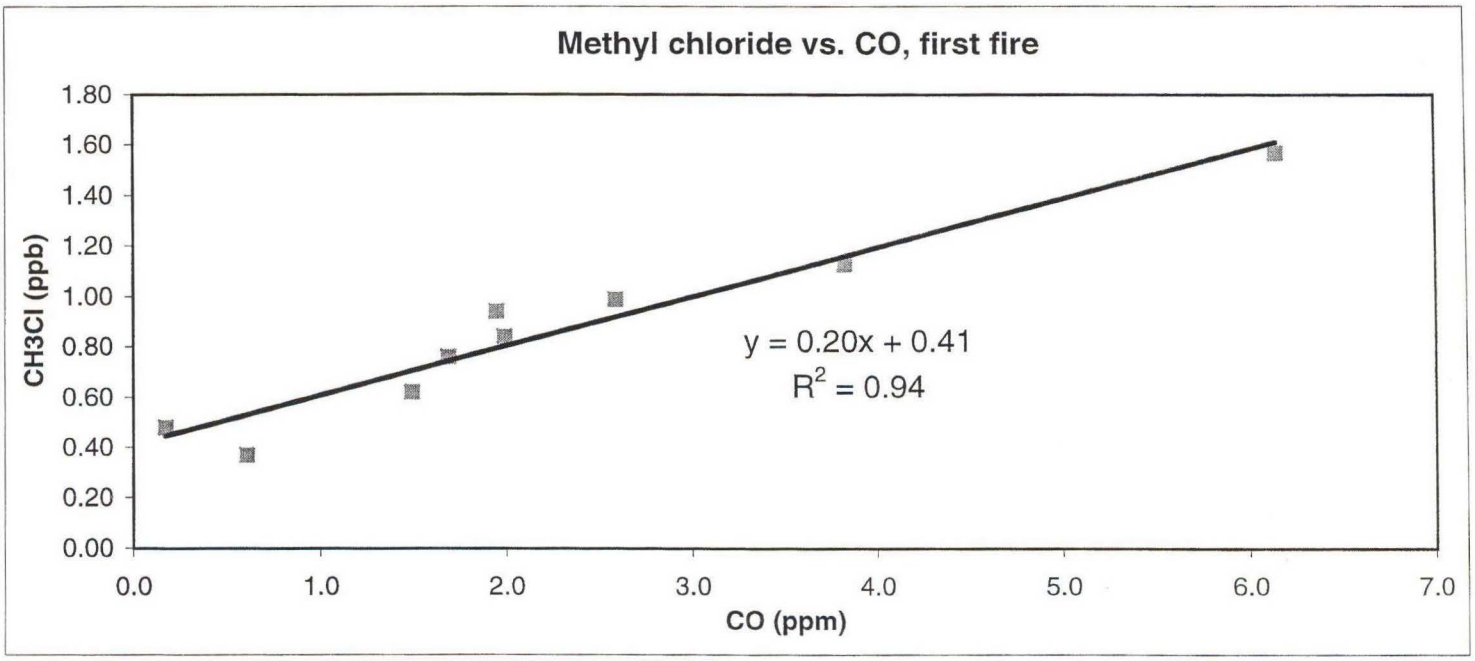
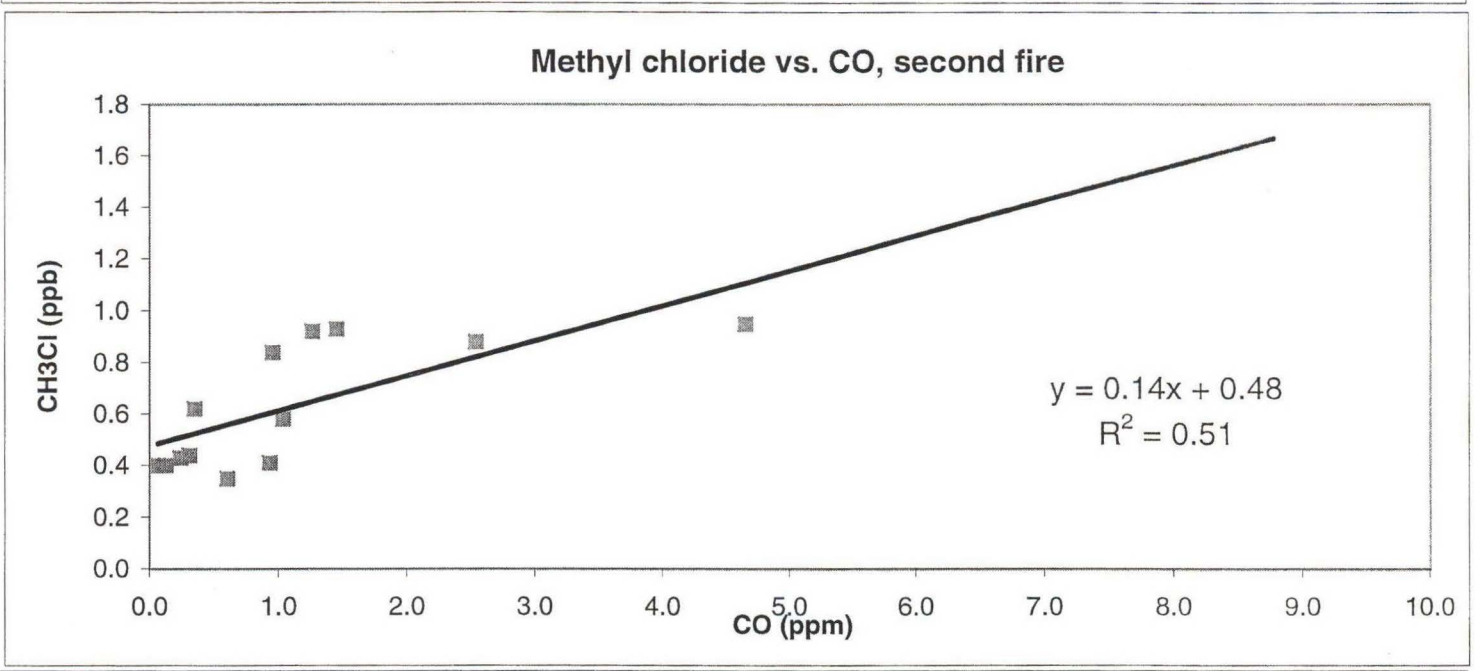


Figure 7. Fort Steward Fires. AirCraft Canisters.





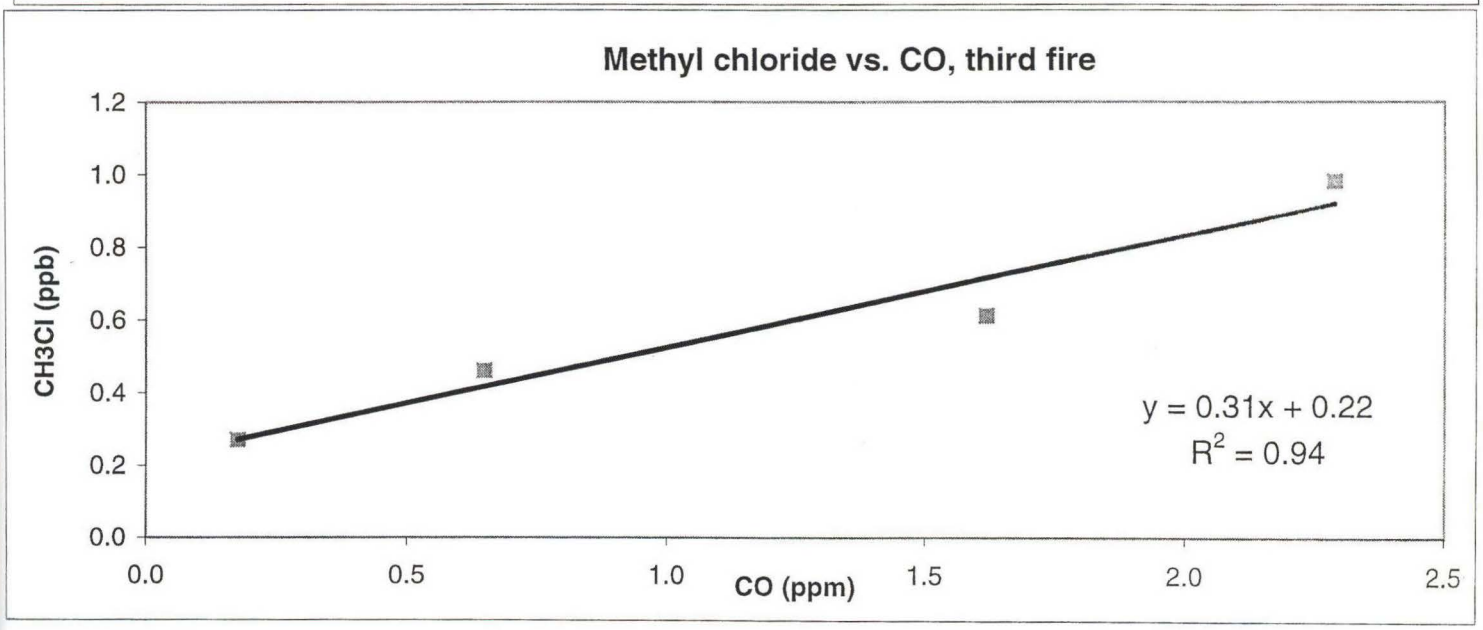
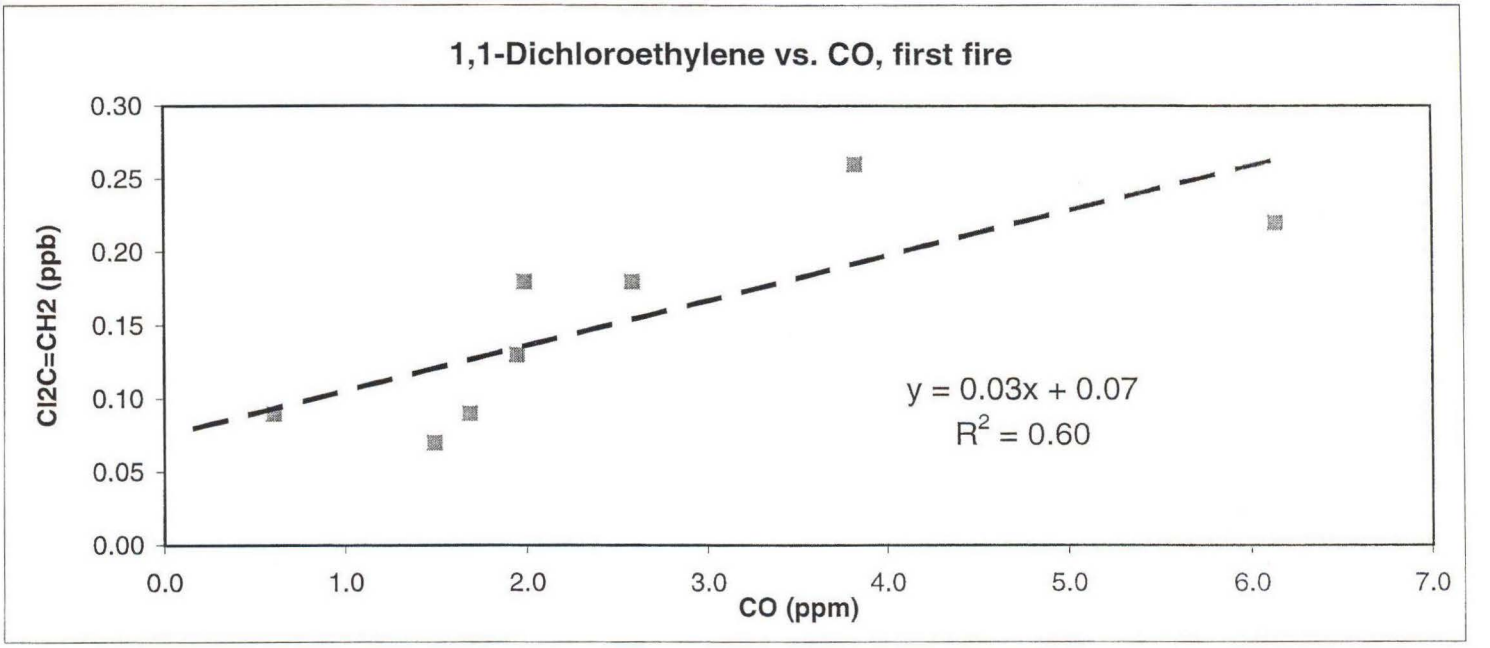


Figure 8. Fort Steward Fires. AirCraft Canisters.



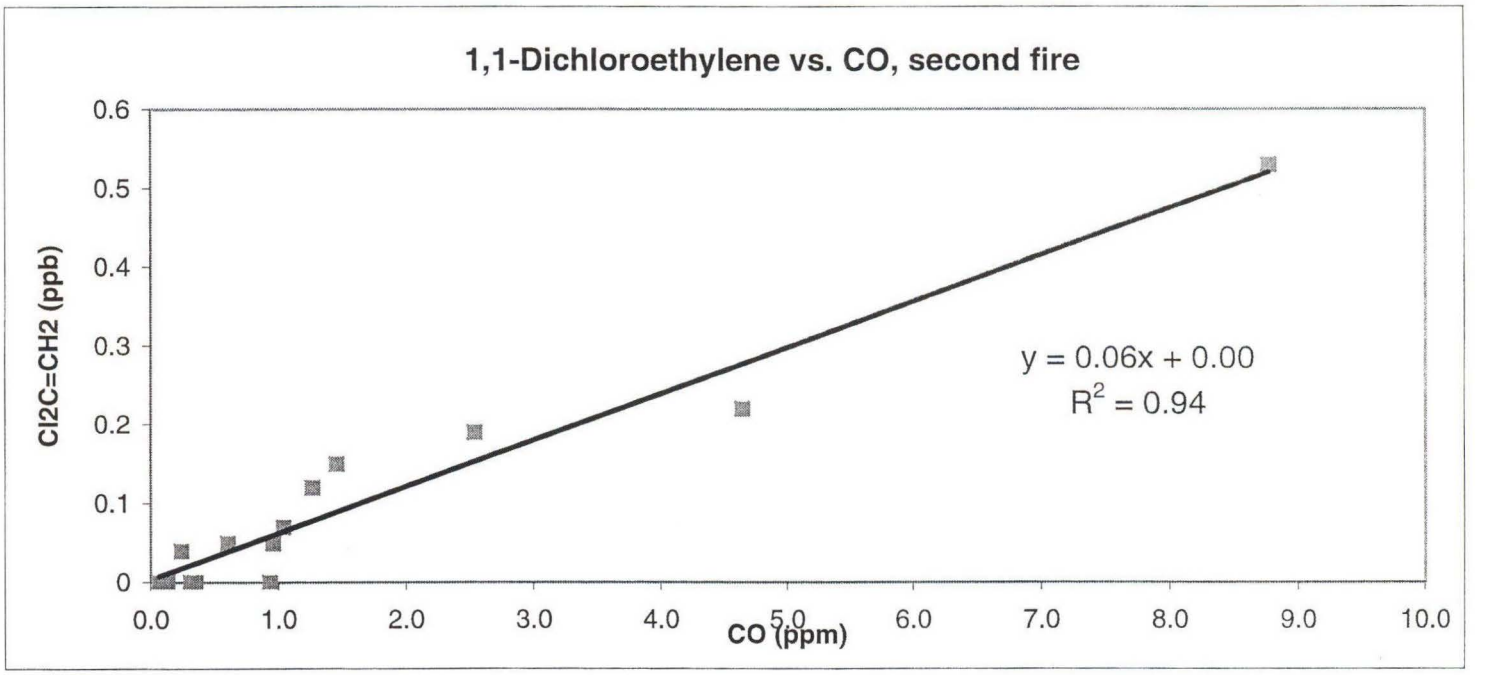


Figure 9. Fort Steward Fires. AirCraft Canisters.

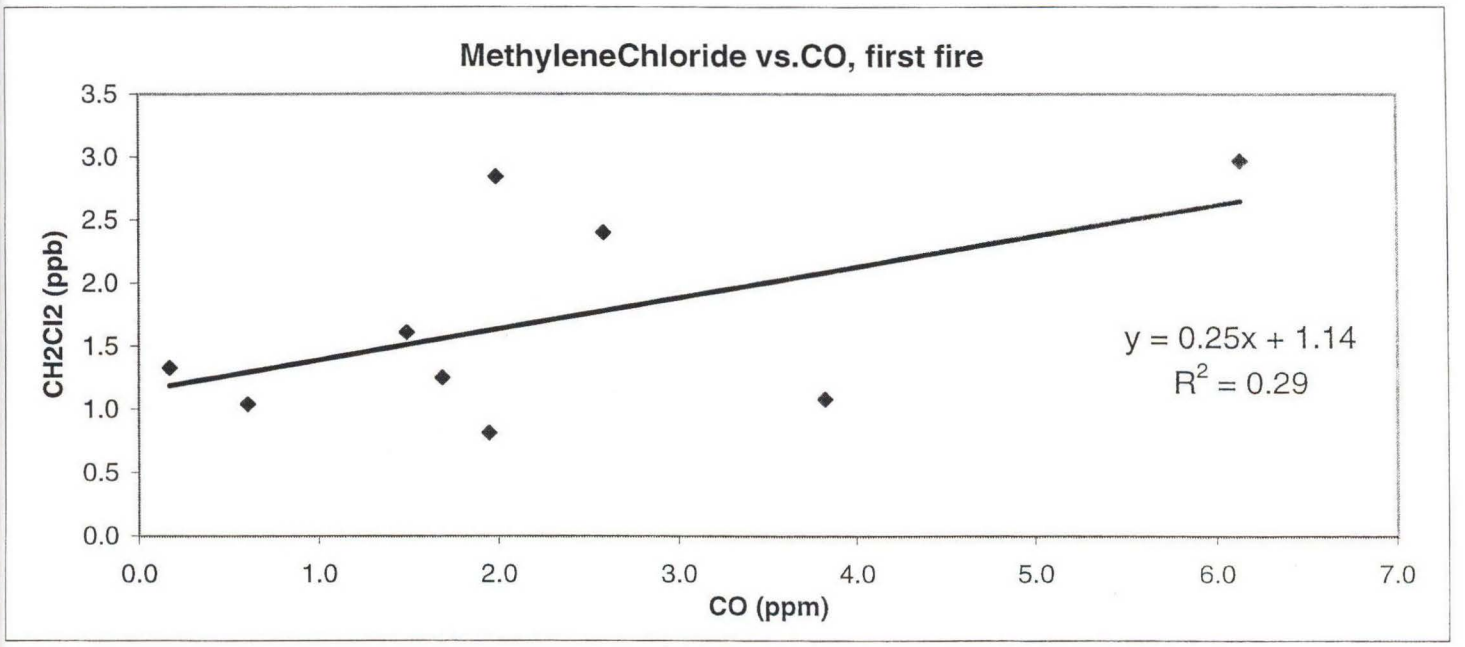
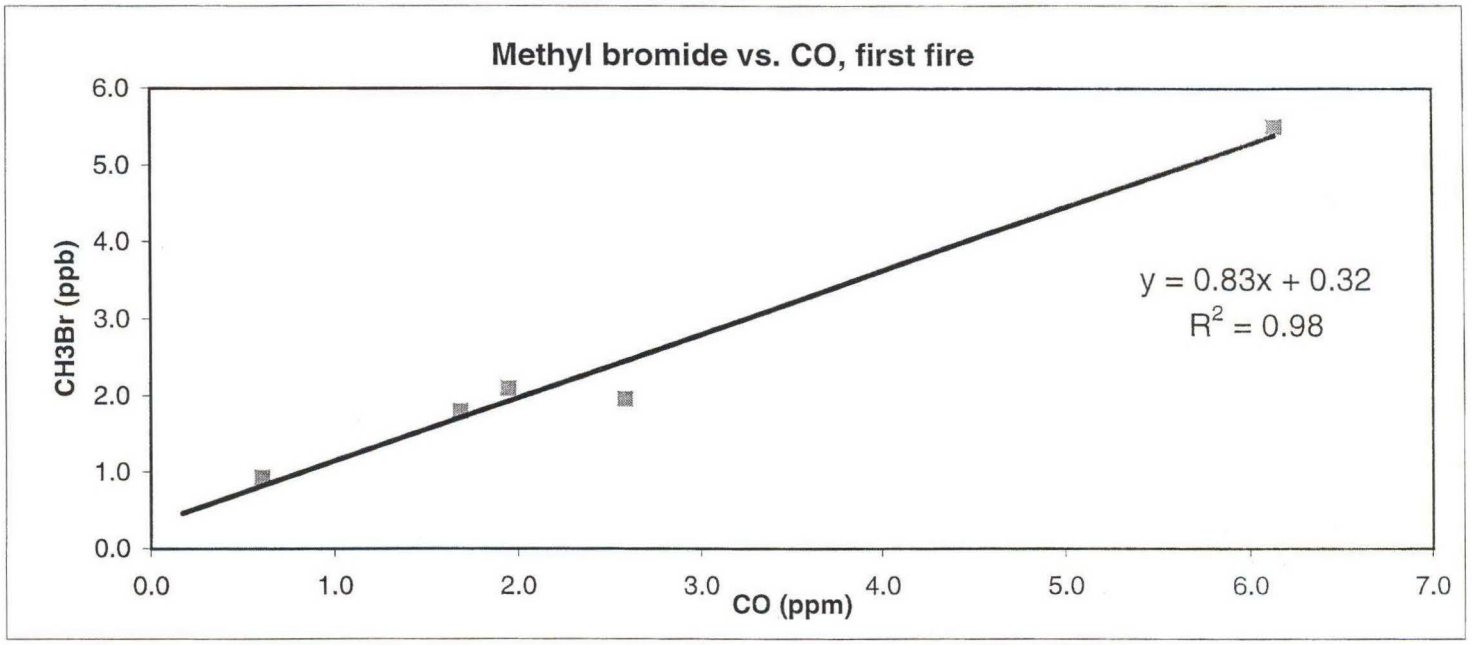
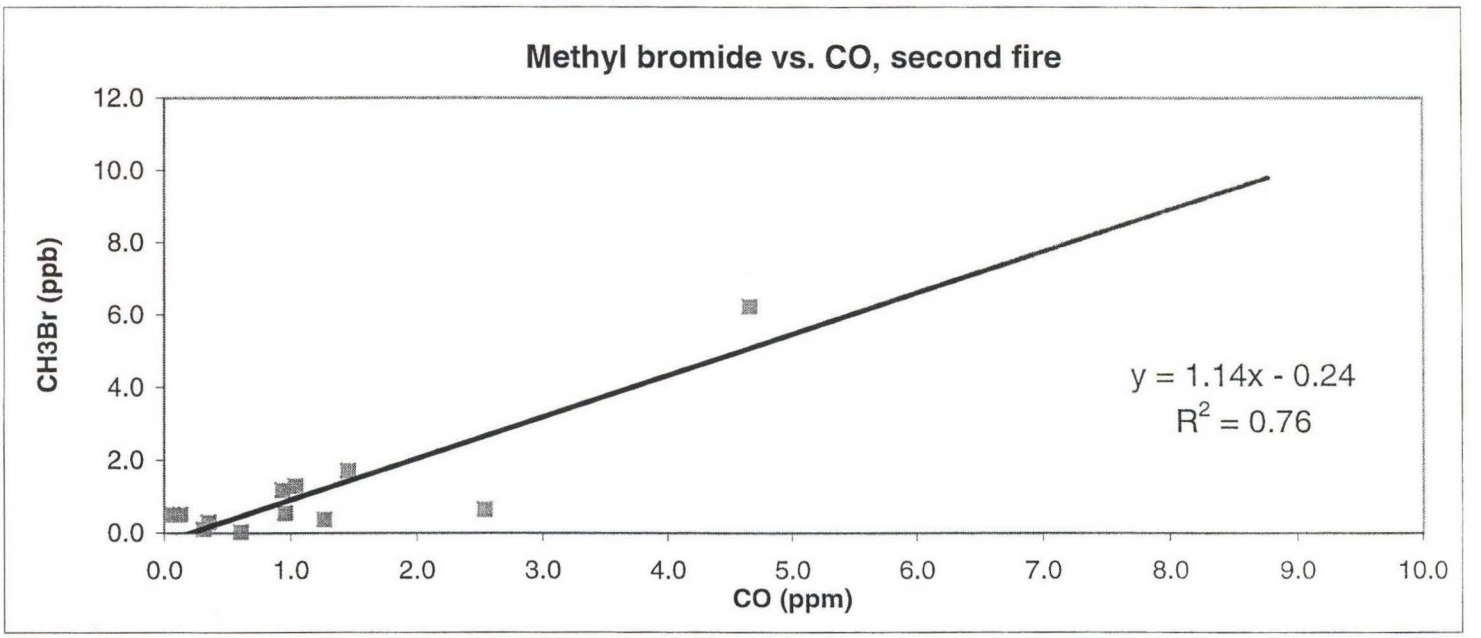


Figure 10. Fort Steward Fires. AirCraft Canisters.





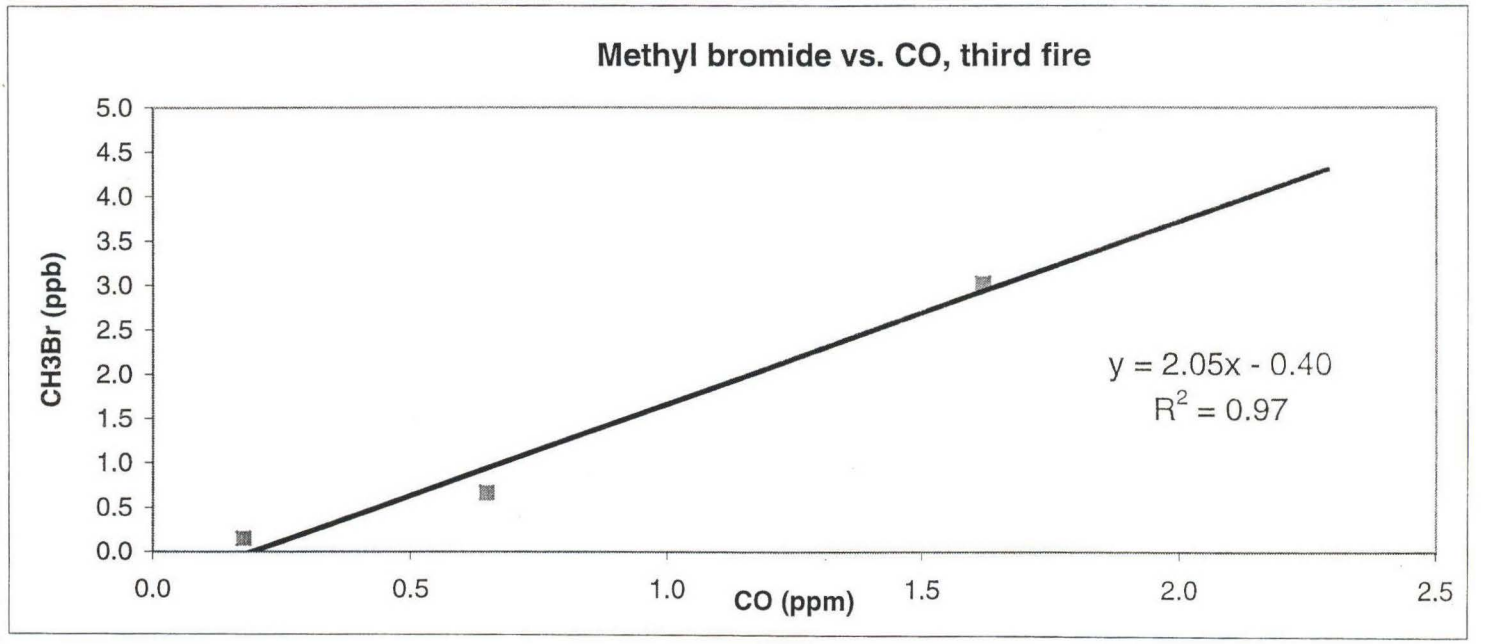
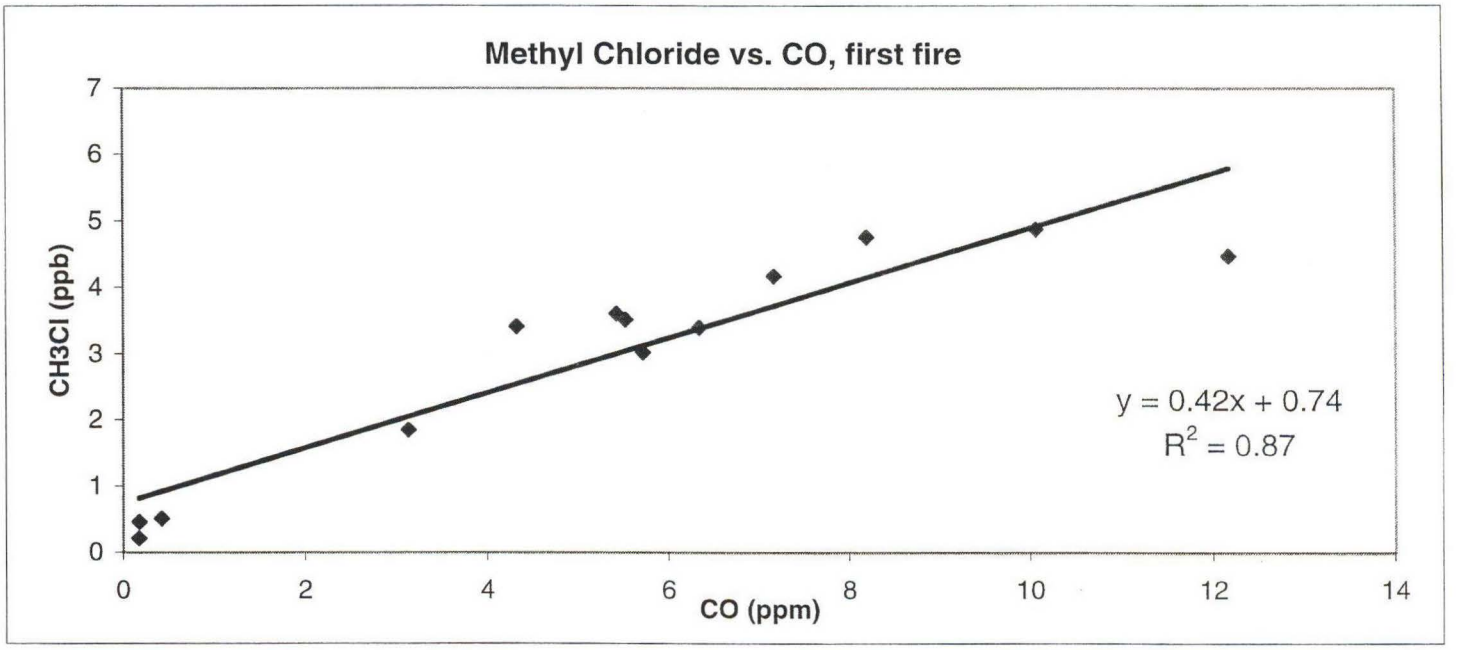
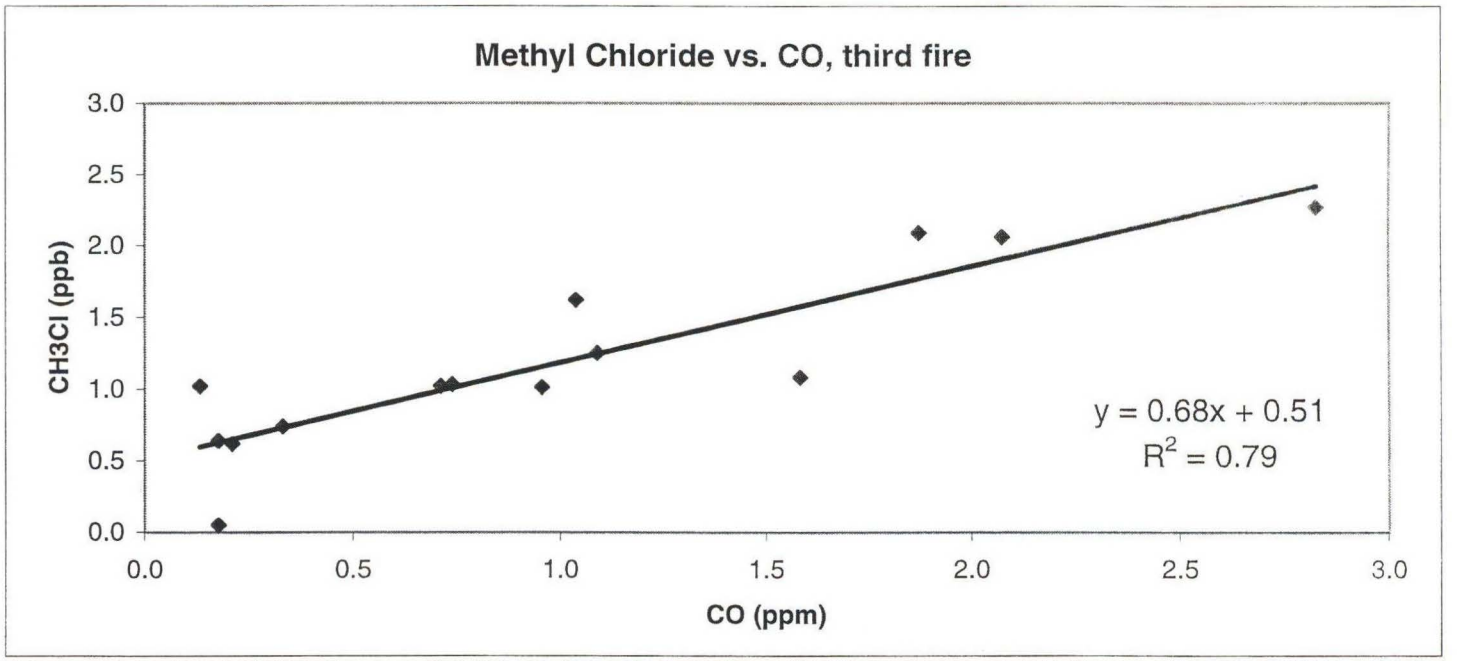


Figure 11. Camp LeJeune Fires. AirCraft Canisters.





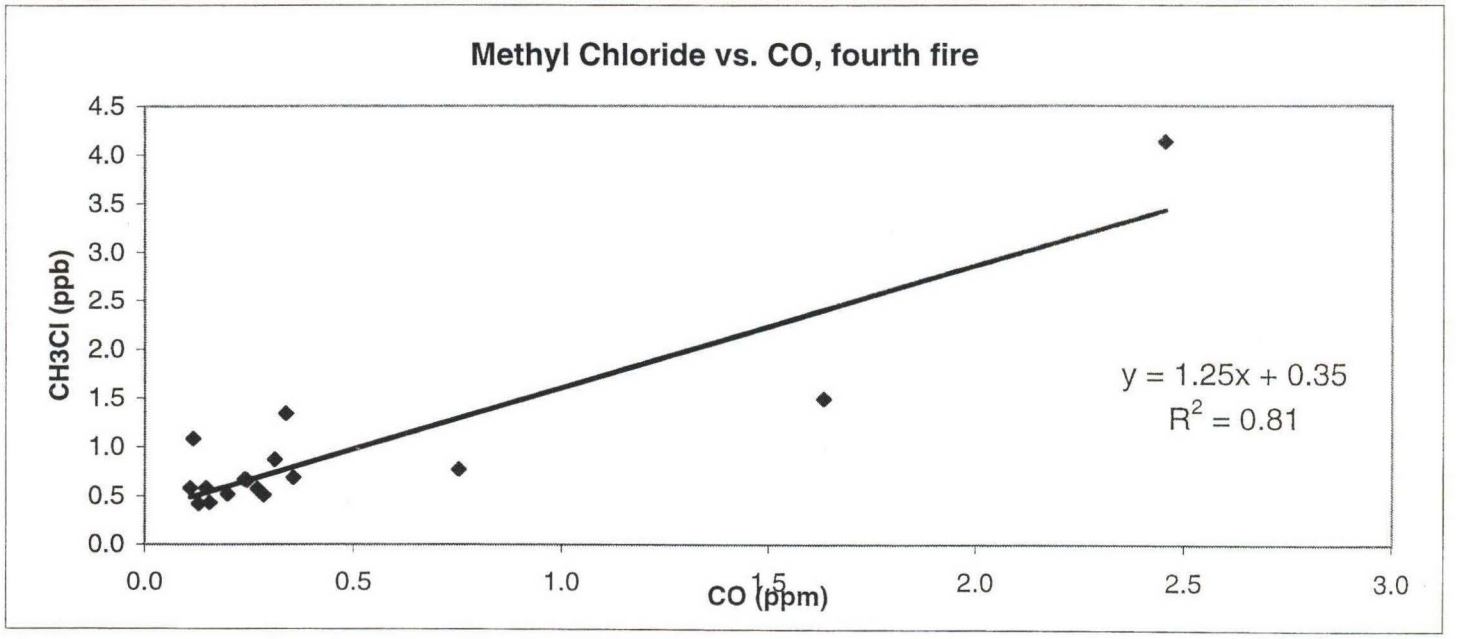
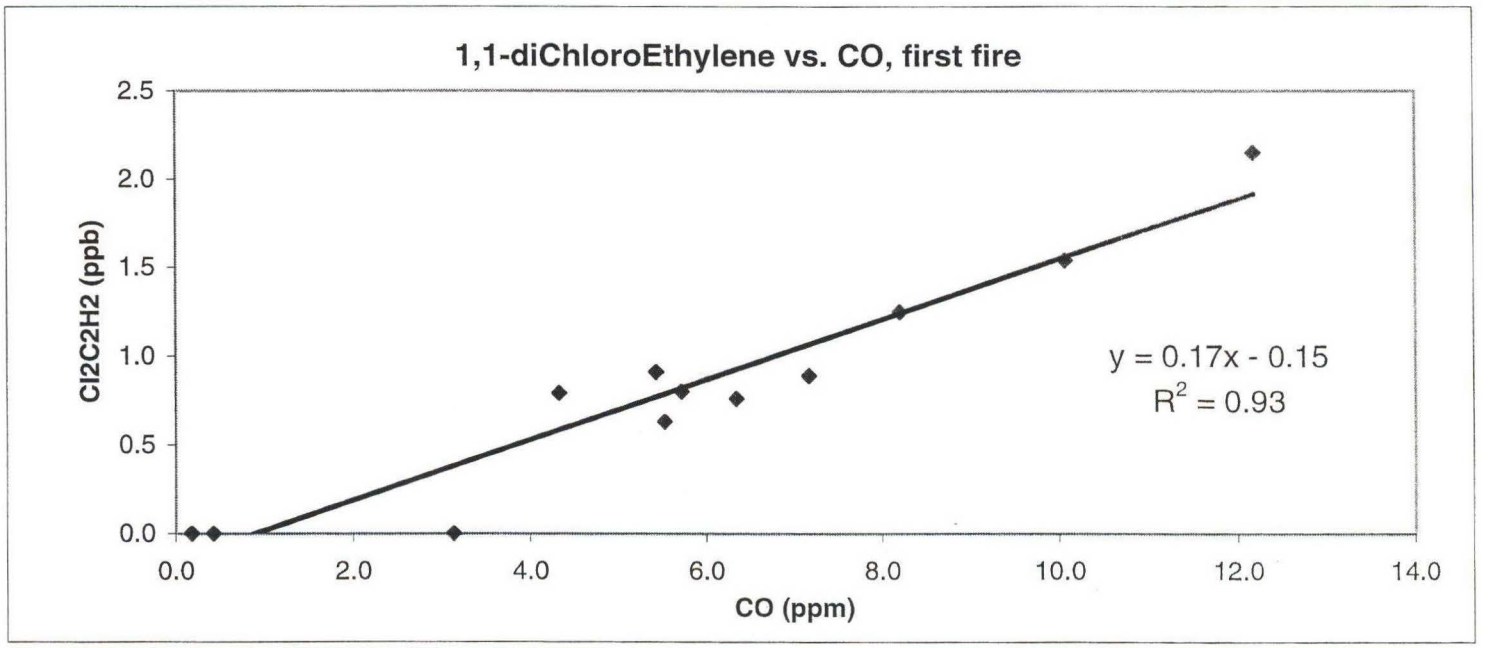
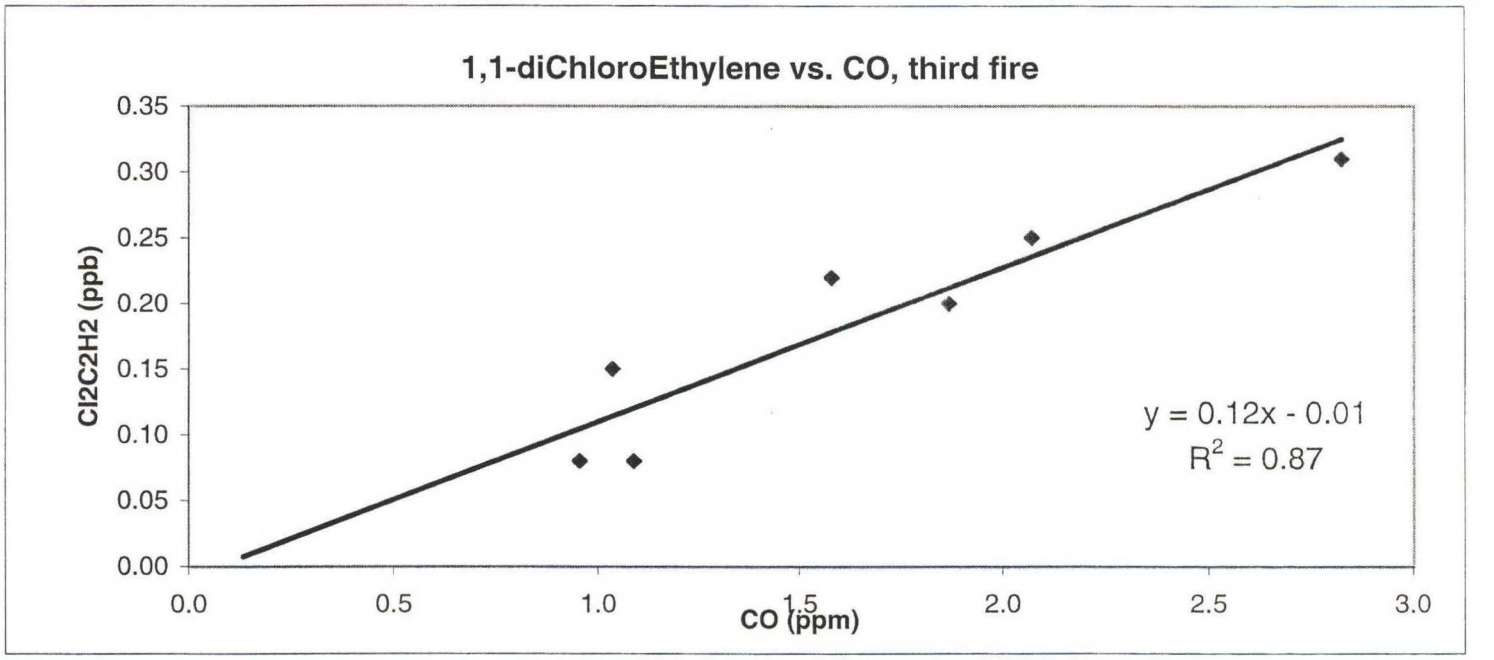


Figure 12. Camp LeJeune Fires. AirCraft Canisters.





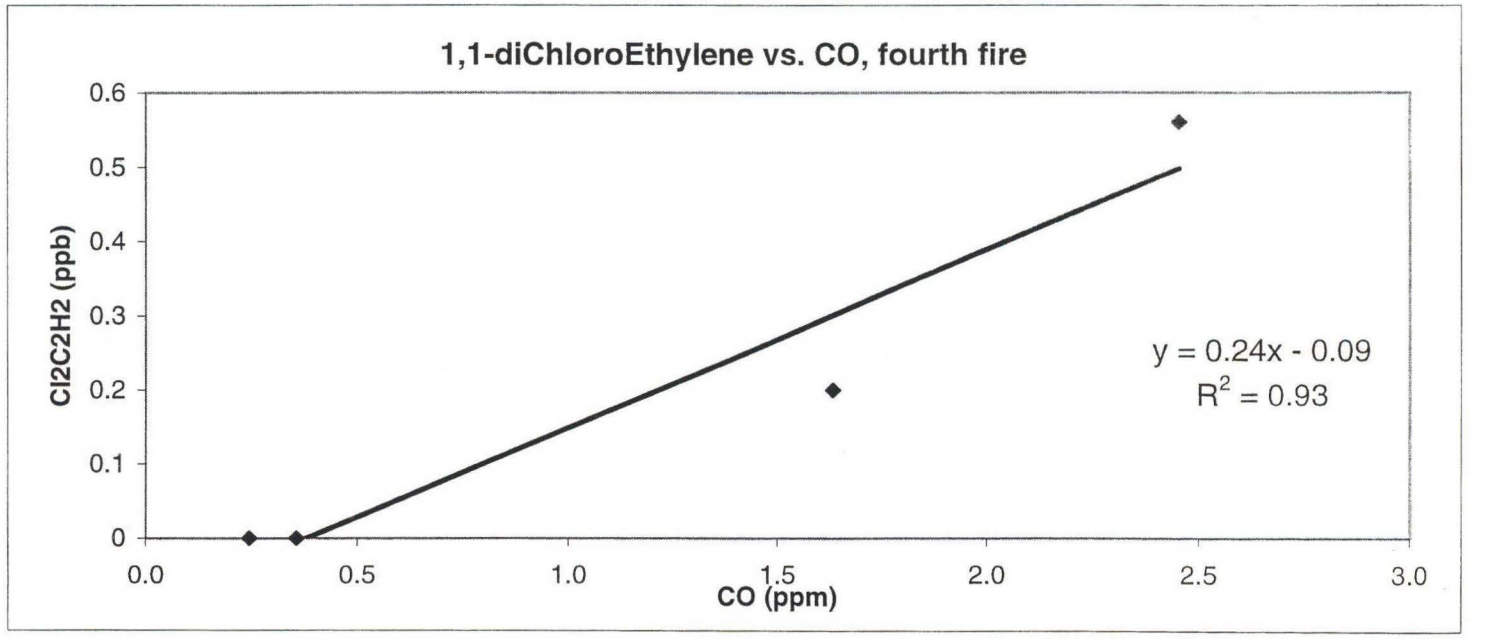
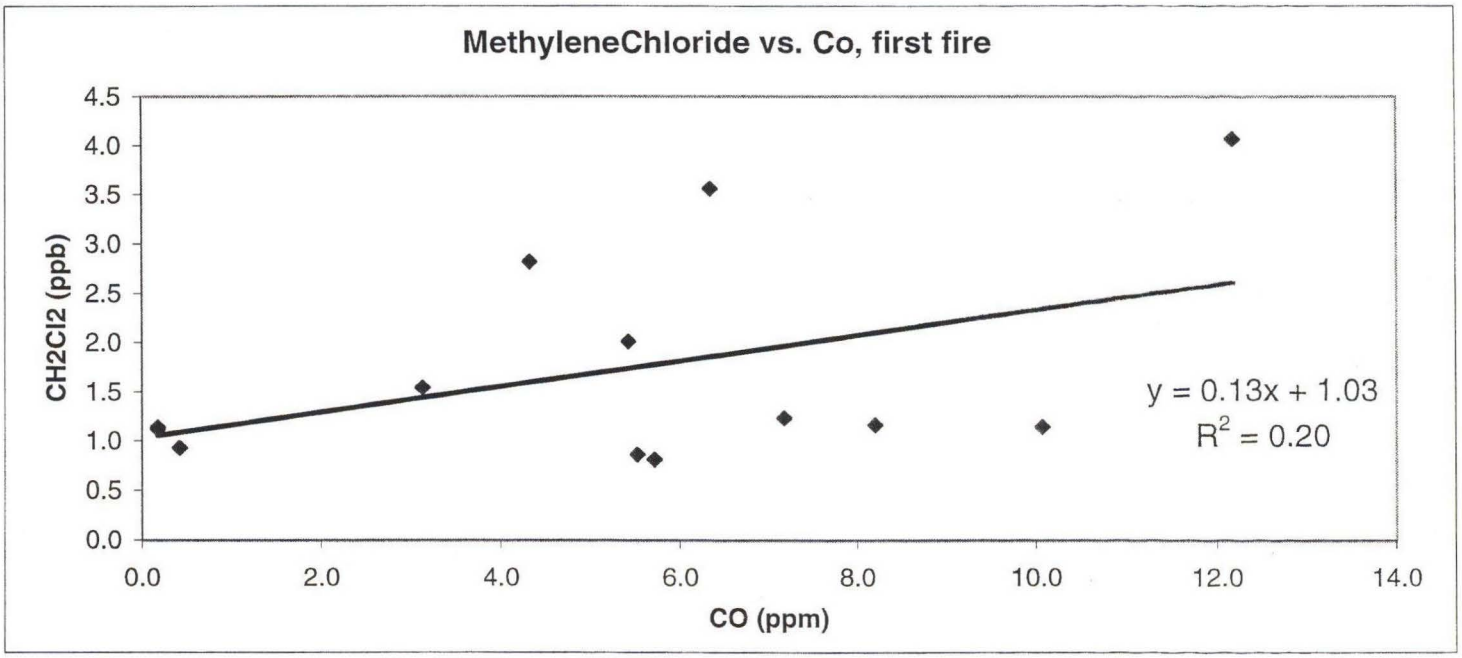


Figure 13. Camp LeJeune Fires. AirCraft Canisters.



Only the Fort Stewart data show a strong correlation with methyl bromide (Figure10). Why this compound was only measured in significant quantity at Fort Stewart and not the other southeast sites is unclear. It may be due to high vegetation content at Fort Stewart or possibly due to the type of fires there. For methylene chloride no strong correlations were found. Very high levels of this gas were found in all the canisters, possibly due to the utilization of methylene chloride to clean the aircraft, (the concentrations of methylene chloride were measured higher than methyl chloride). The results of the regressions with CO are presented in Table 2.

Table 2. Canister Results Summary for the Southeast United States.

Southeast US 1997 Aircraft Canister Results- Halogenated gases vs. CO (r^2)									
	Eglin AFB, FL			Ft. Stewart, GA			Camp Lejeune, NC		
combustion efficiency	.99	.89	.96	1.0	1.0	1.0	.93	1.0	1.0
number of canisters	11	9	9	9	14	4	13	16	16
above background concentration		6	5	7	8	3	10	10	3
methyl chloride	-	.76	.66	.94	.51	.94	.87	.79	.81
methyl bromide	-			.97	.76	.97	.24		-
1,1-dichloroethene	.	.92	.90	.52	.94	-	.93	.87	.93
methylene chloride	-			.29	-		.20		-
chloroform	-						-		
1,1,1-trichloroethane	-						-		
carbon tetrachloride	-						-		

3. Alaska Fires

There were 5 fires in Alaska that were sampled by aircraft. The first fire had very low concentrations that were about the same as background. The concentrations of halogens compounds in the samples were lower than the Zambia fires and typical of high altitude diluted concentrations.

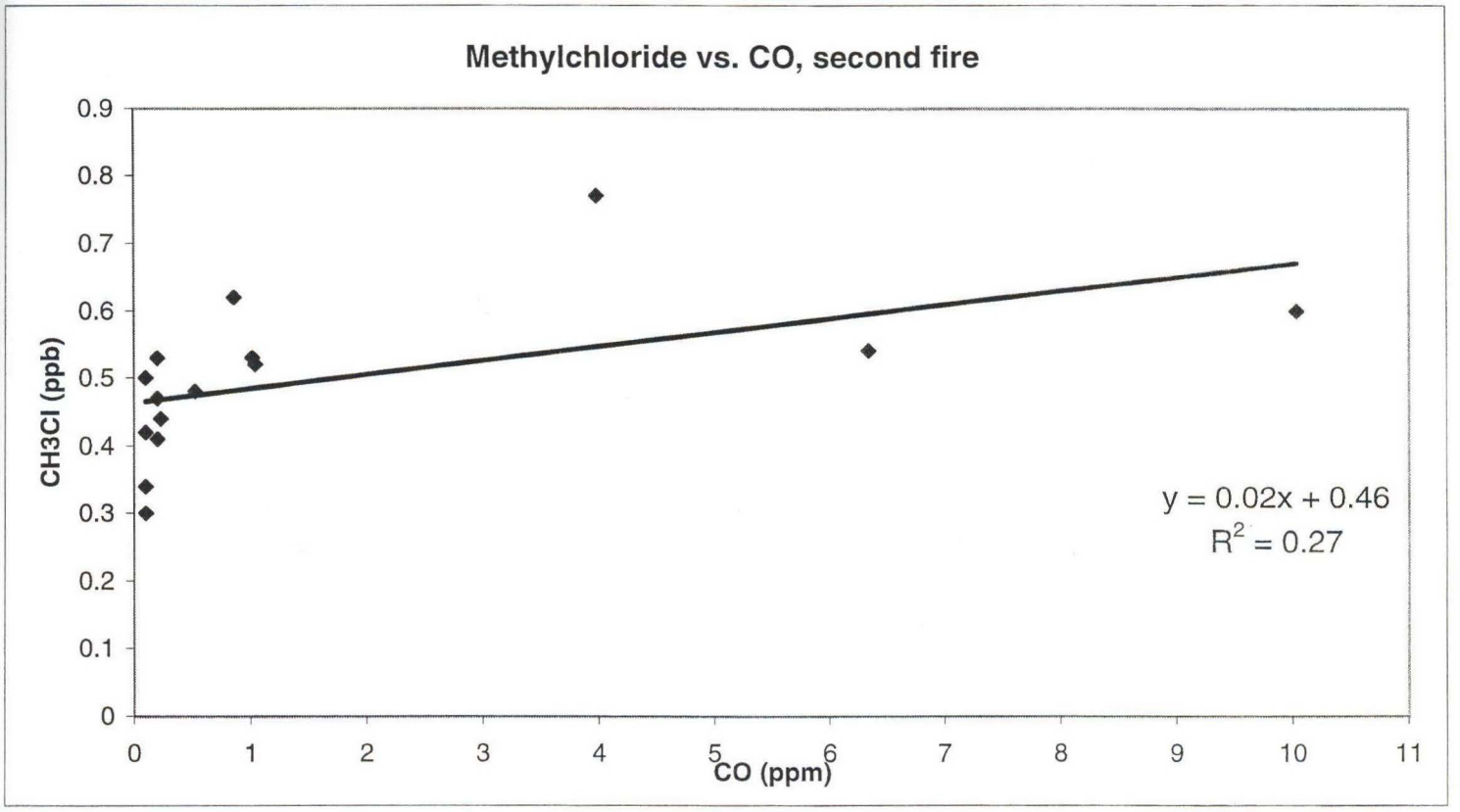
The samples were free of interfering compounds and therefore the identification and quantification of halogenated compounds was good. The concentrations of 1,1,1-trichloroethane, carbontetrachloride and chloroform were at background level for all fires.

Linear correlation with CO: For the first fire all of the canister samples were at background concentrations except for one canister, therefore, no correlations could be established (Table 3). For all the other Alaska fires, a high degree of correlation for methyl chloride and methylene chloride with CO was found (Figures 14-20). This was is in contrast to the southeast samples where methylene chloride was at a high constant level and indicates this halocarbon may be an important emission from biomass burning. Only the second and third fires show a correlation with 1,1-dichloroethylene, but the number of samples above the limit of detection are small (4 data for the second fire and 2 data for the third fire). For the other fires, the 1,1-dichloroethylene concentrations were mostly at the limit of detection of the E.C.D.

Table 3. Alaska 1997 Canister Results

Alaska 1997 Aircraft Canister Results- Halogenated gases vs. CO (r^2)					
	1st fire	2nd fire	3rd fire	4th fire	5th fire
combustion efficiency	-	.97	.98	.61	.78
number of canisters	8	16	7	15	26
above background concentration	1	6	3	10	12
methyl chloride	-	.27	.61	.65	.64
1,1 dichloroethene	-	.52	.87	-	-
methylene chloride	-	.87	.43	.61	.82
cis-1,2 dichloroethylene	-	-	-	-	-
chloroform	-	-	-	-	-
1,1,1 trichloroethane	-	-	-	-	-
carbon tetrachloride	-	-	-	-	-

Figure 14. Alaska Fires. AirCraft Canisters.



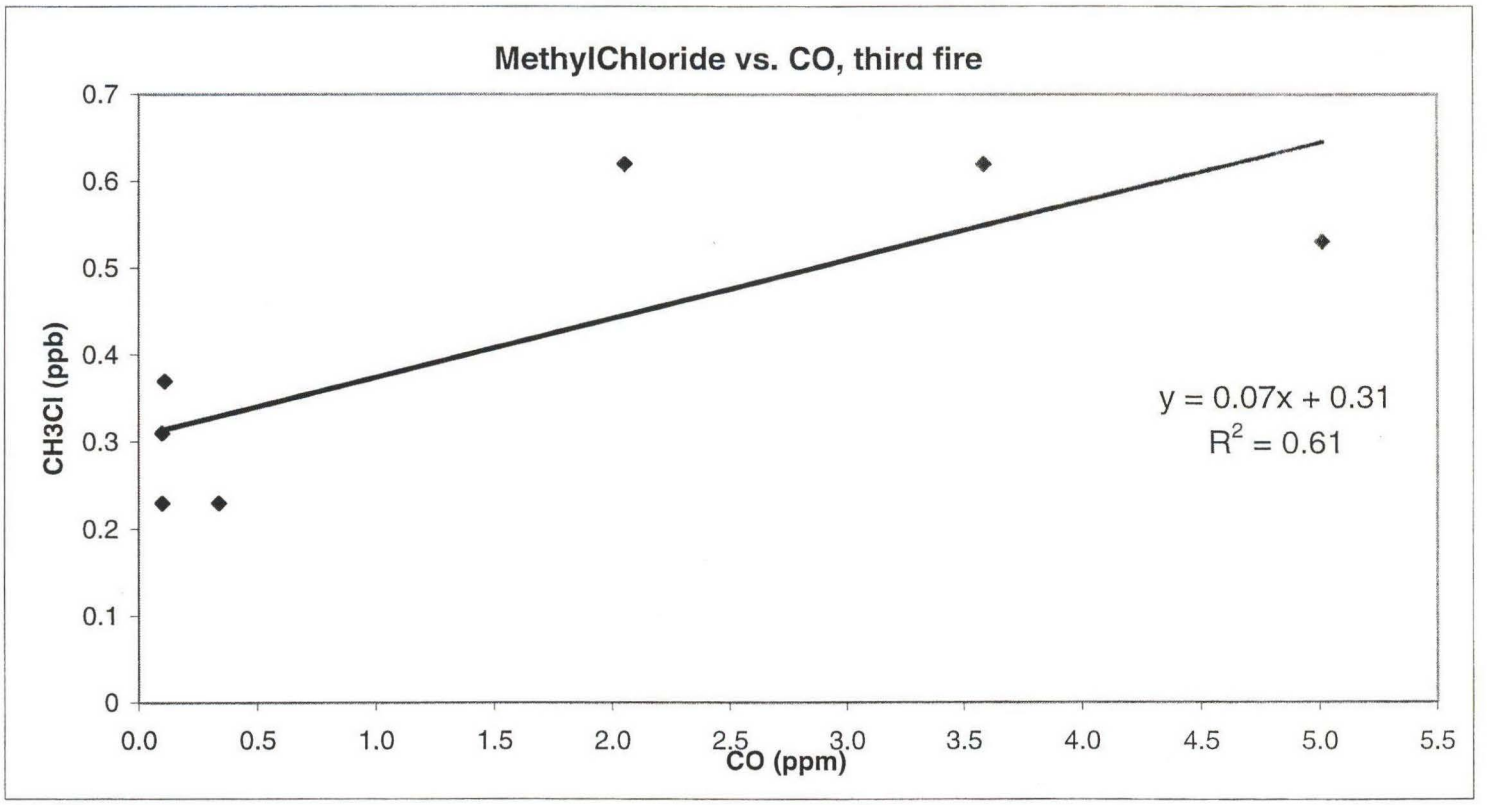
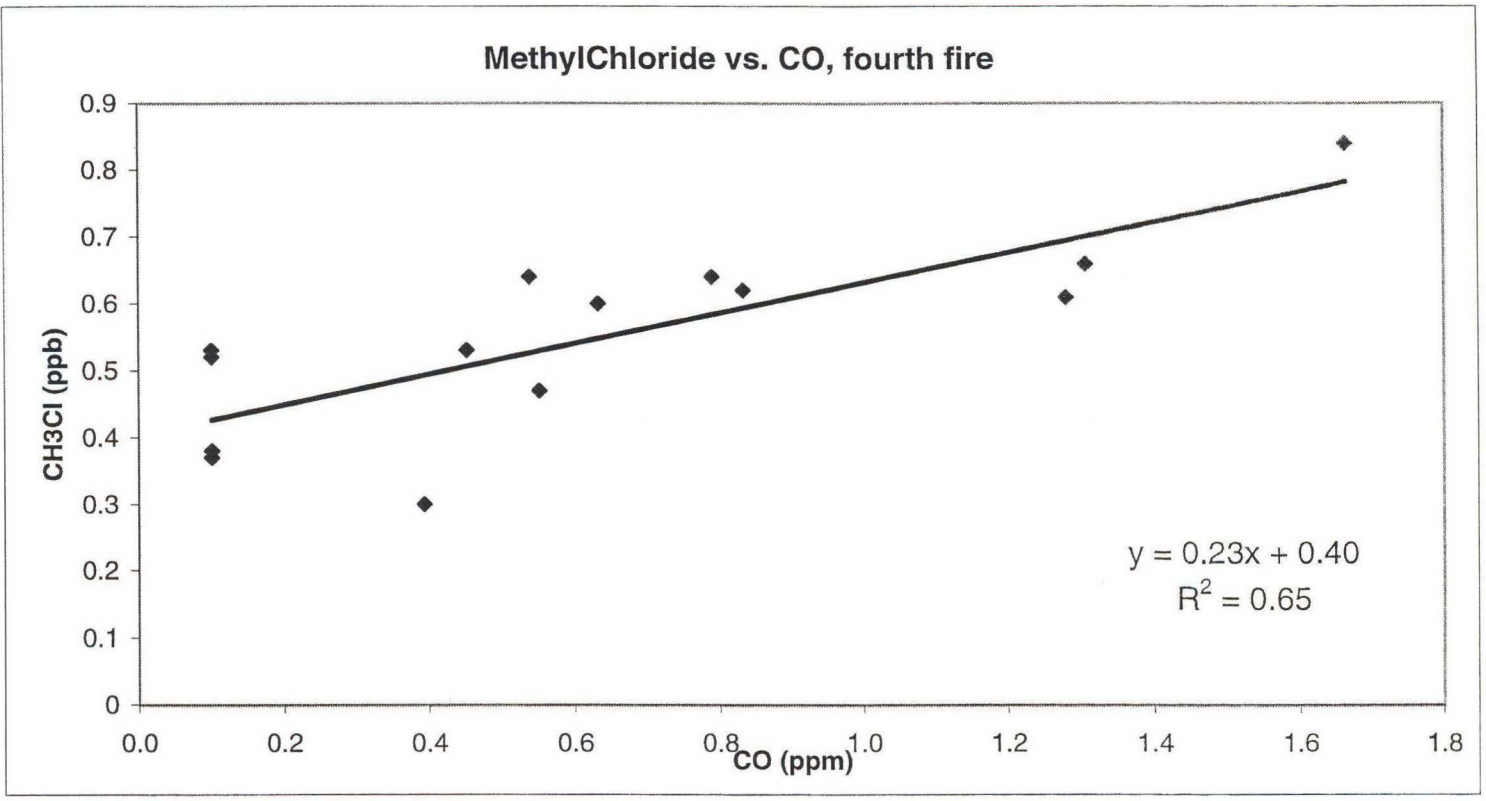


Figure 15. Alaska Fires. AirCraft Canisters.



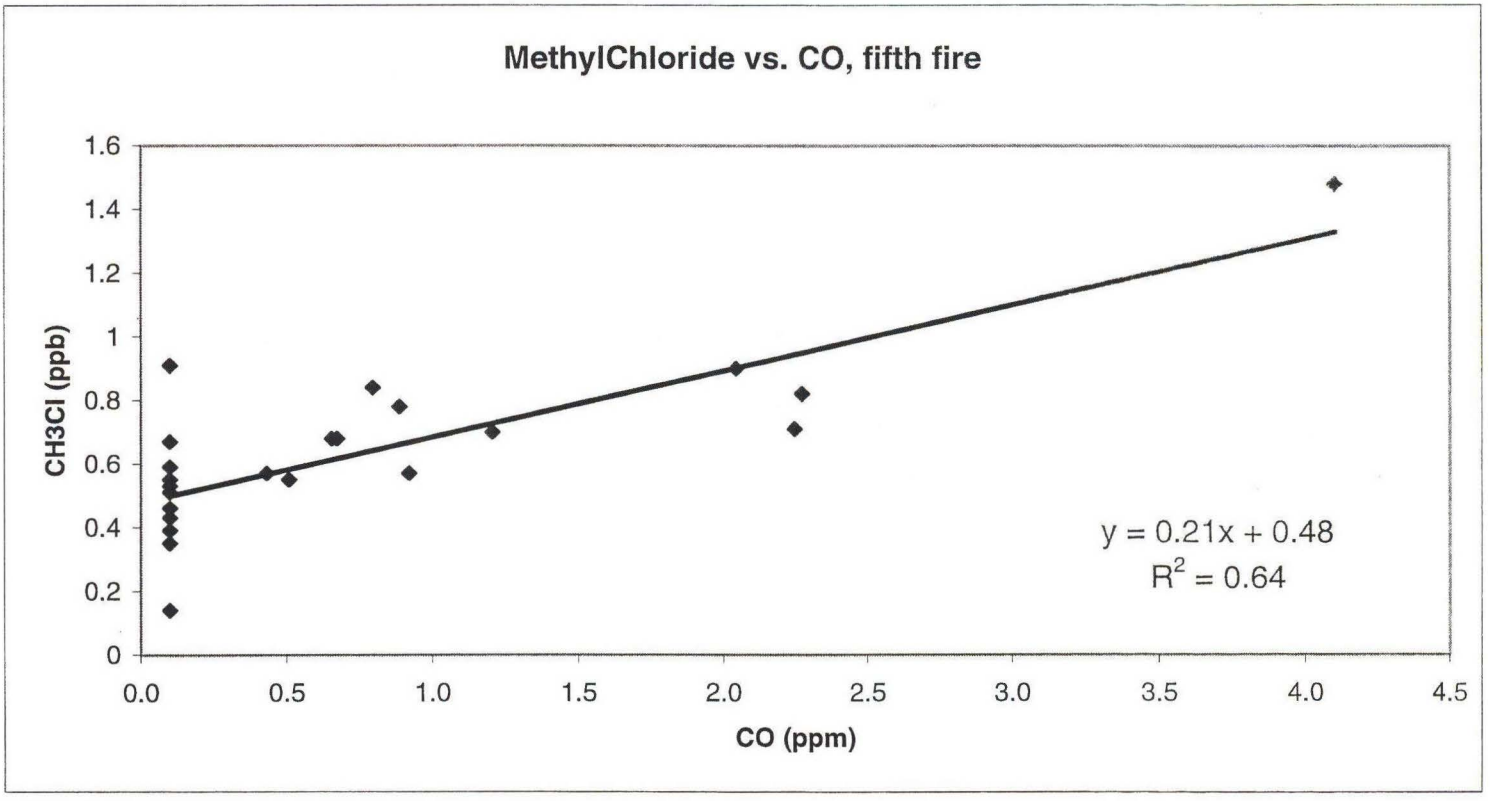
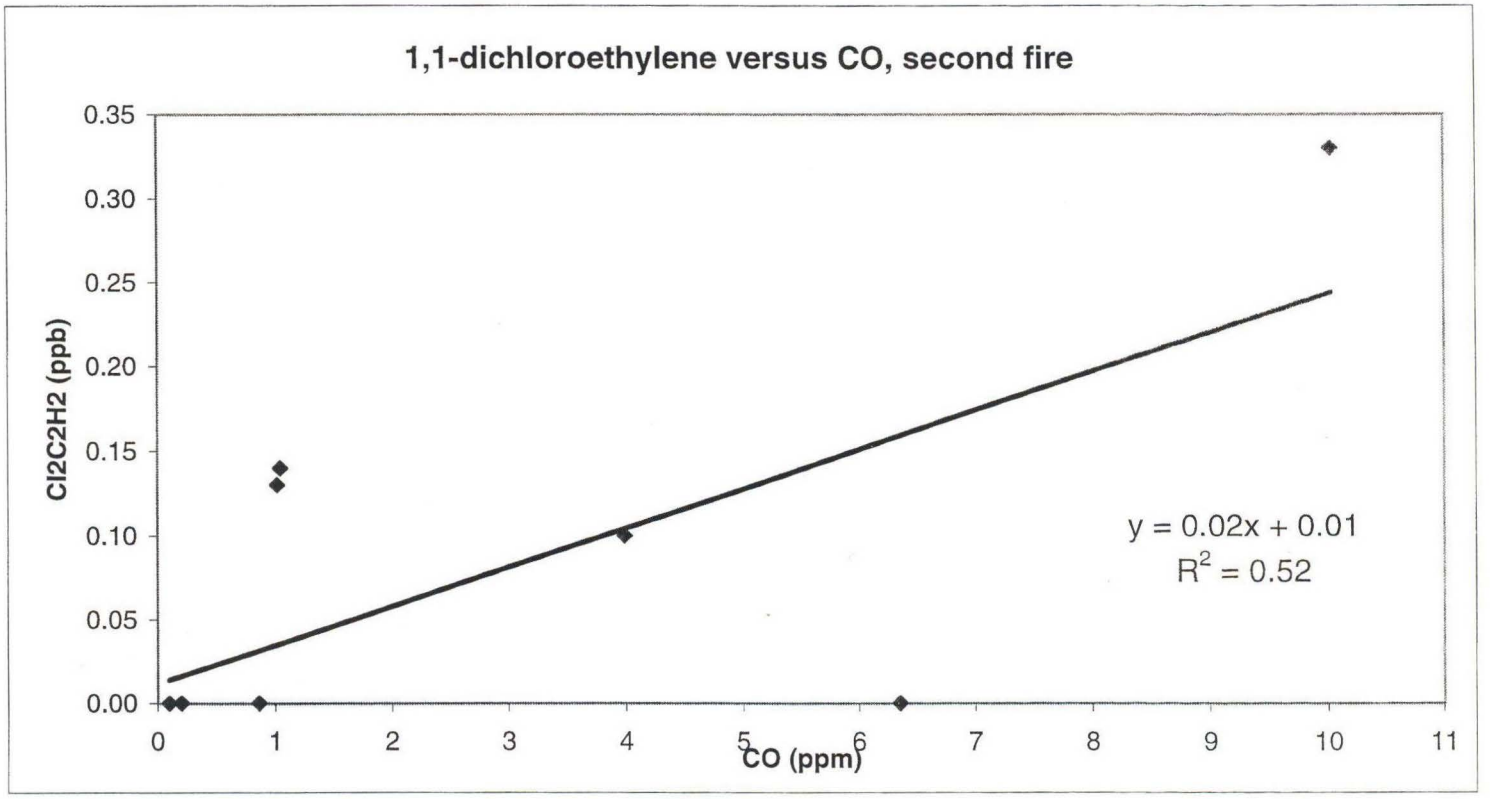


Figure 16. Alaska Fires. AirCraft Canisters.



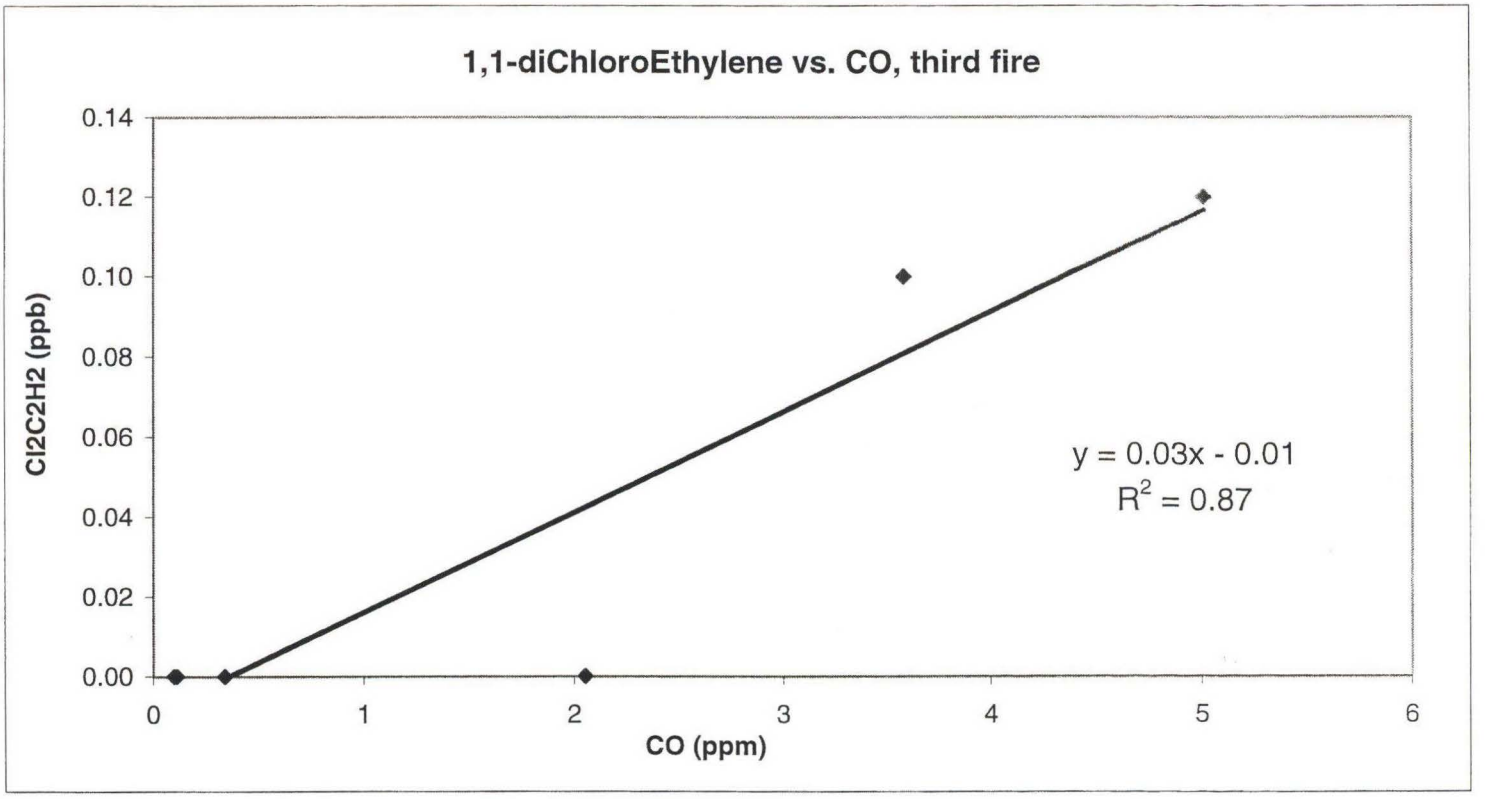
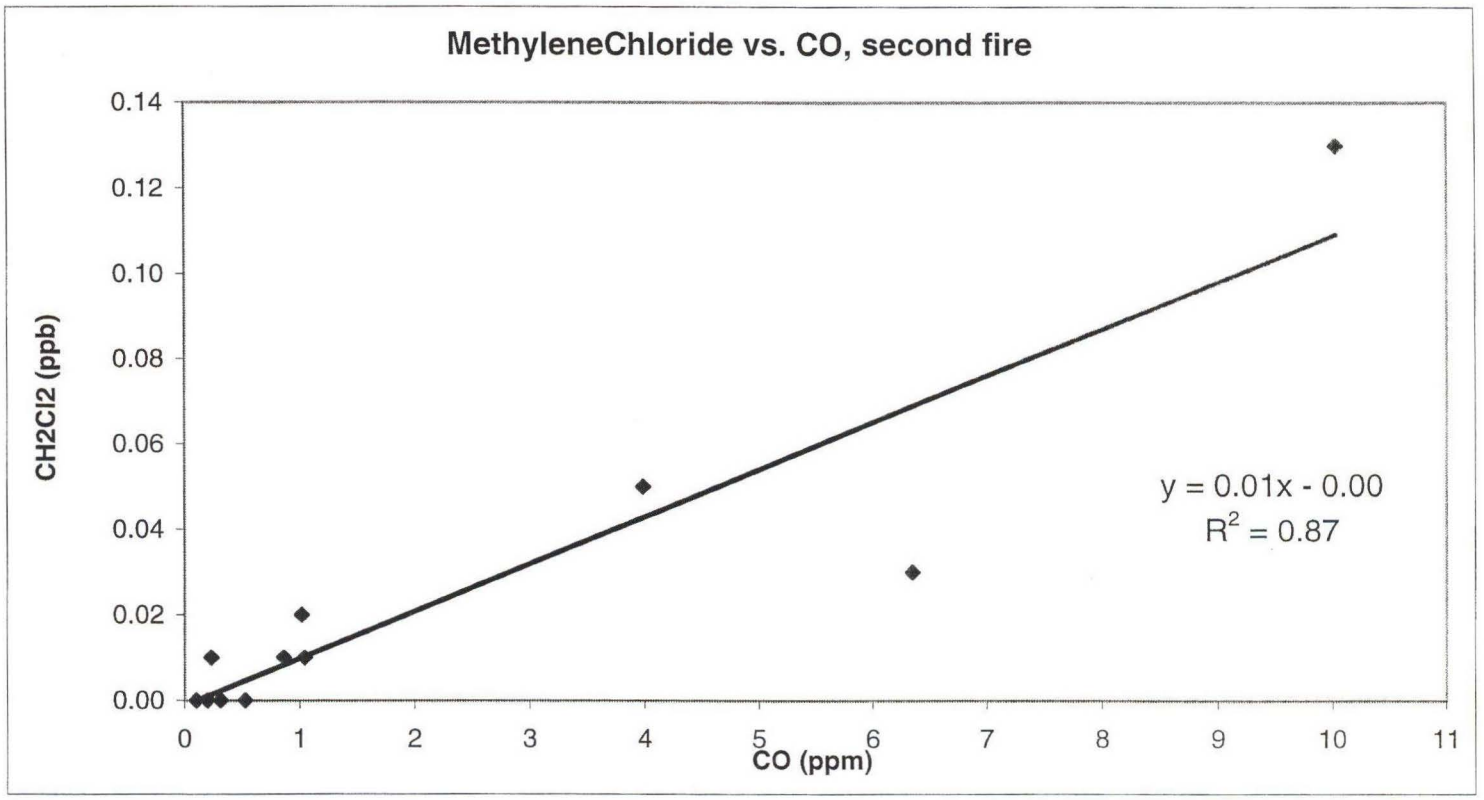


Figure 17. Alaska Fires. AirCraft Canisters.



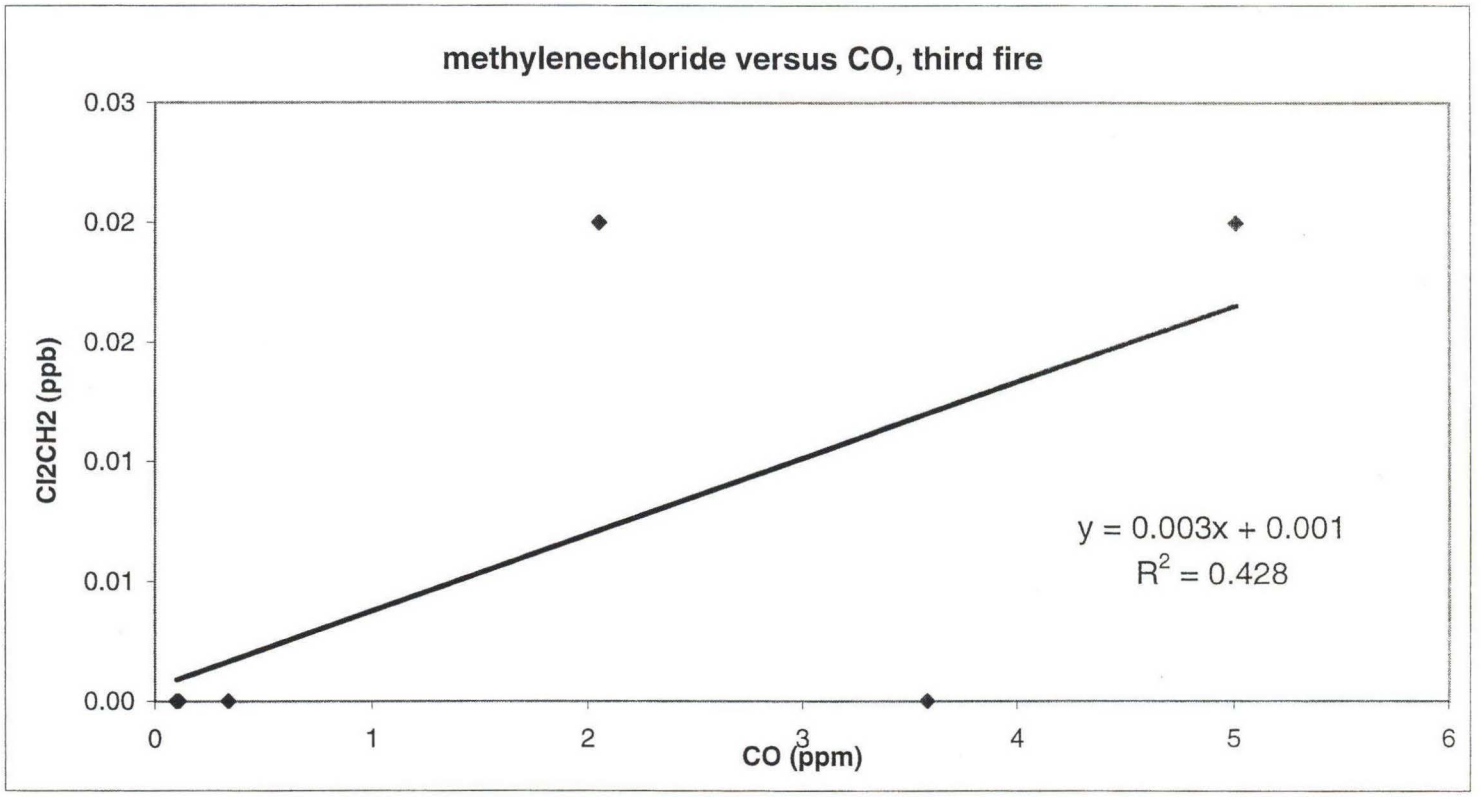
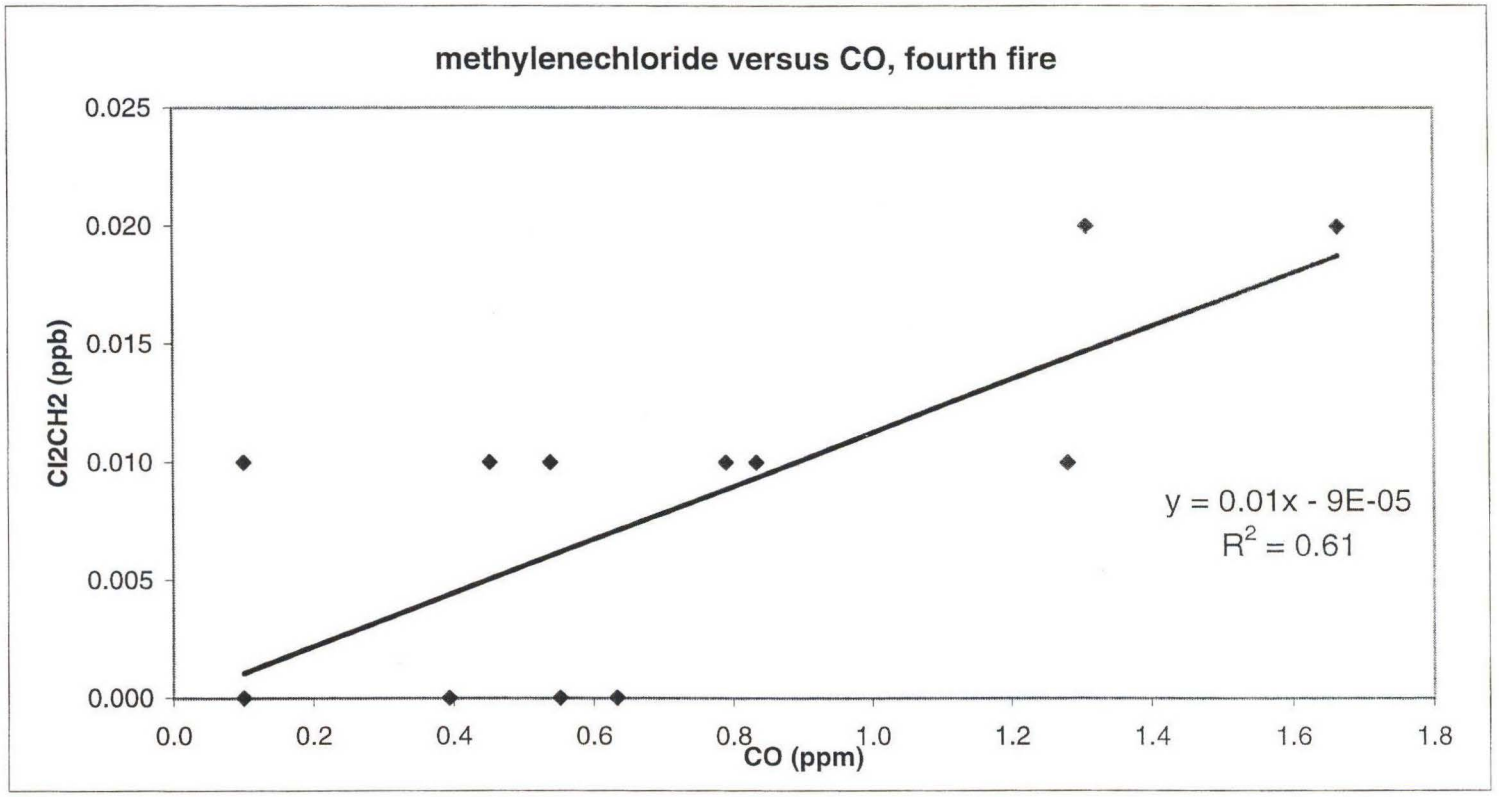


Figure 18. Alaska Fires. AirCraft Canisters.



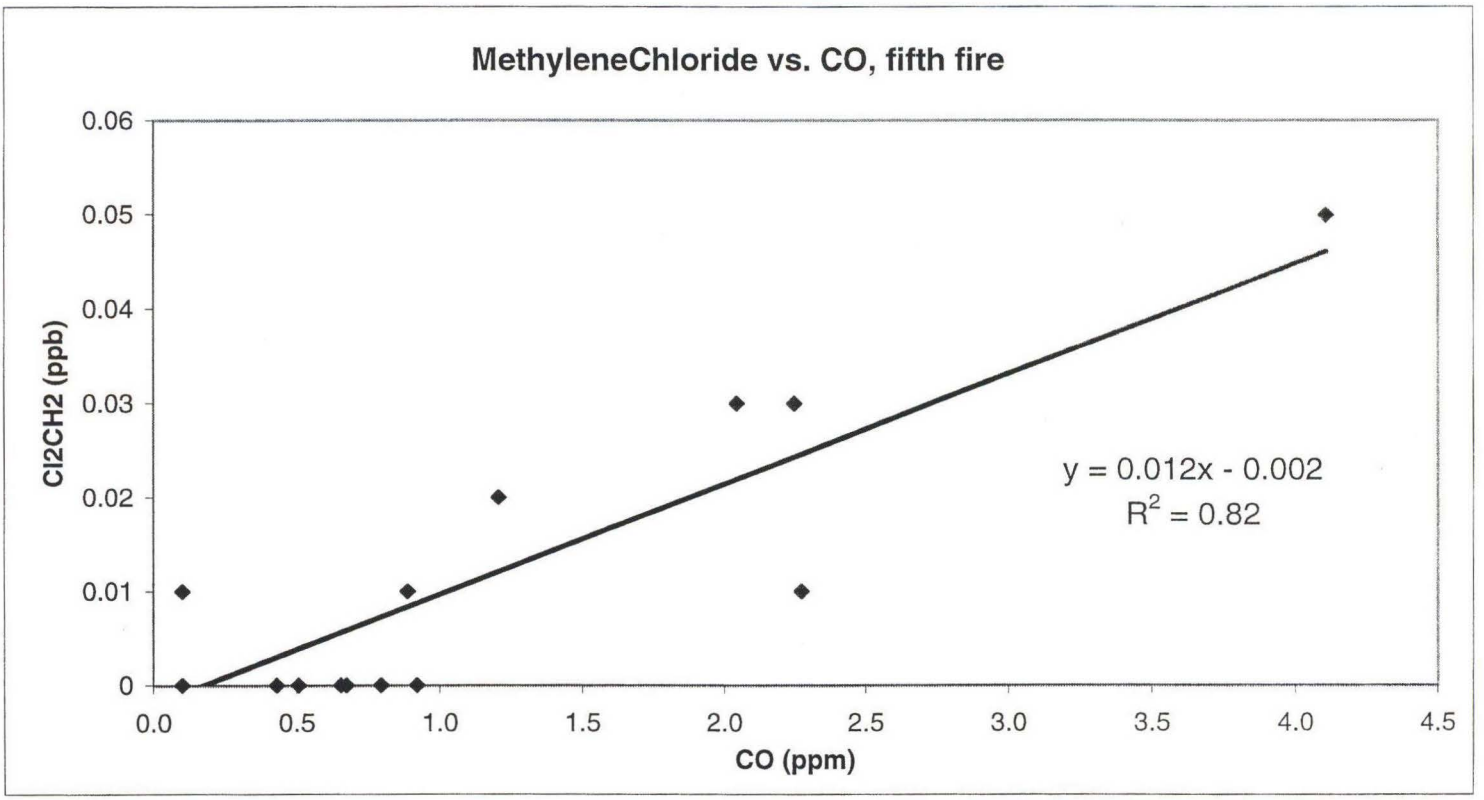
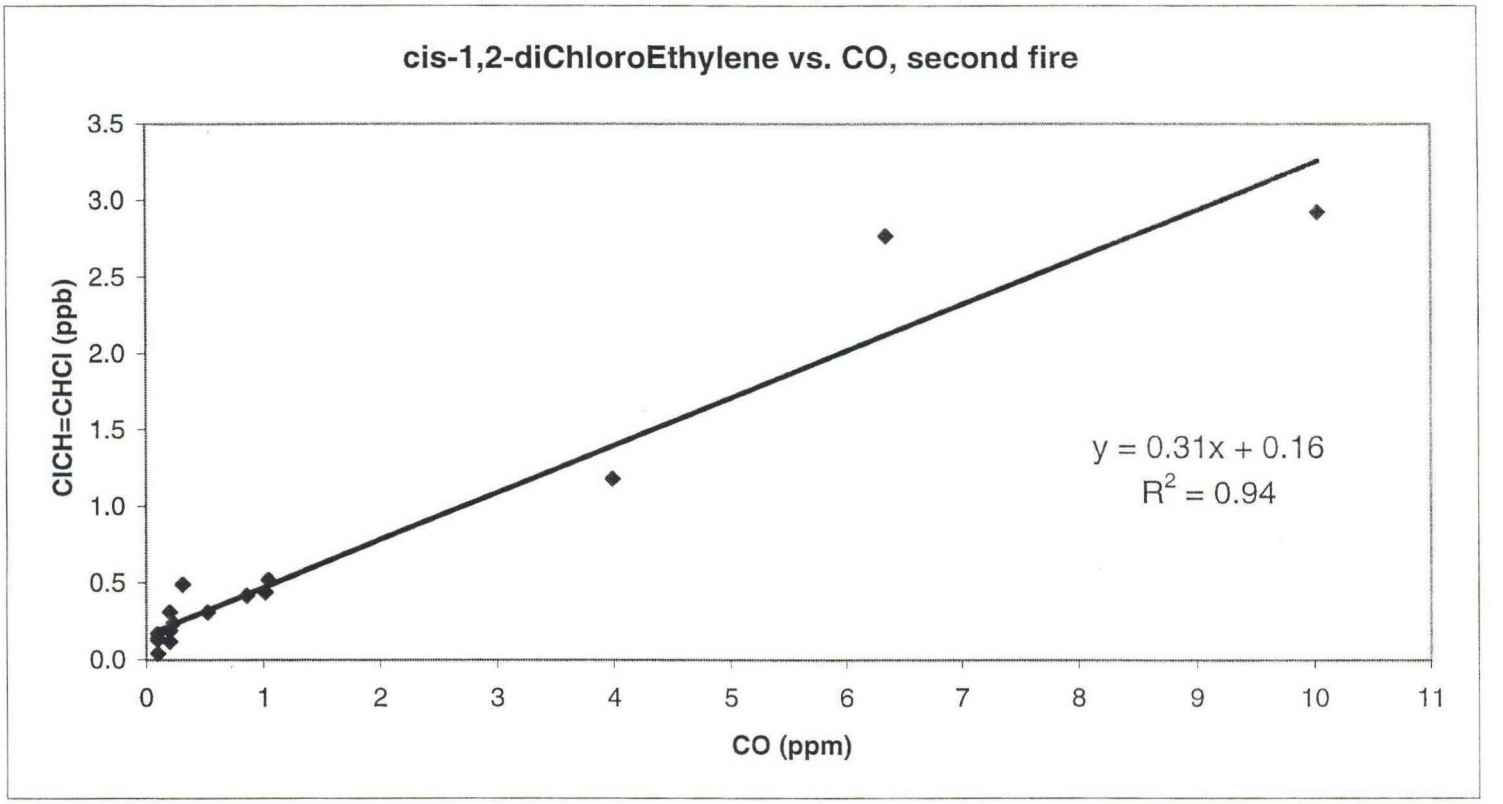


Figure 19. Alaska Fires. AirCraft Canisters.



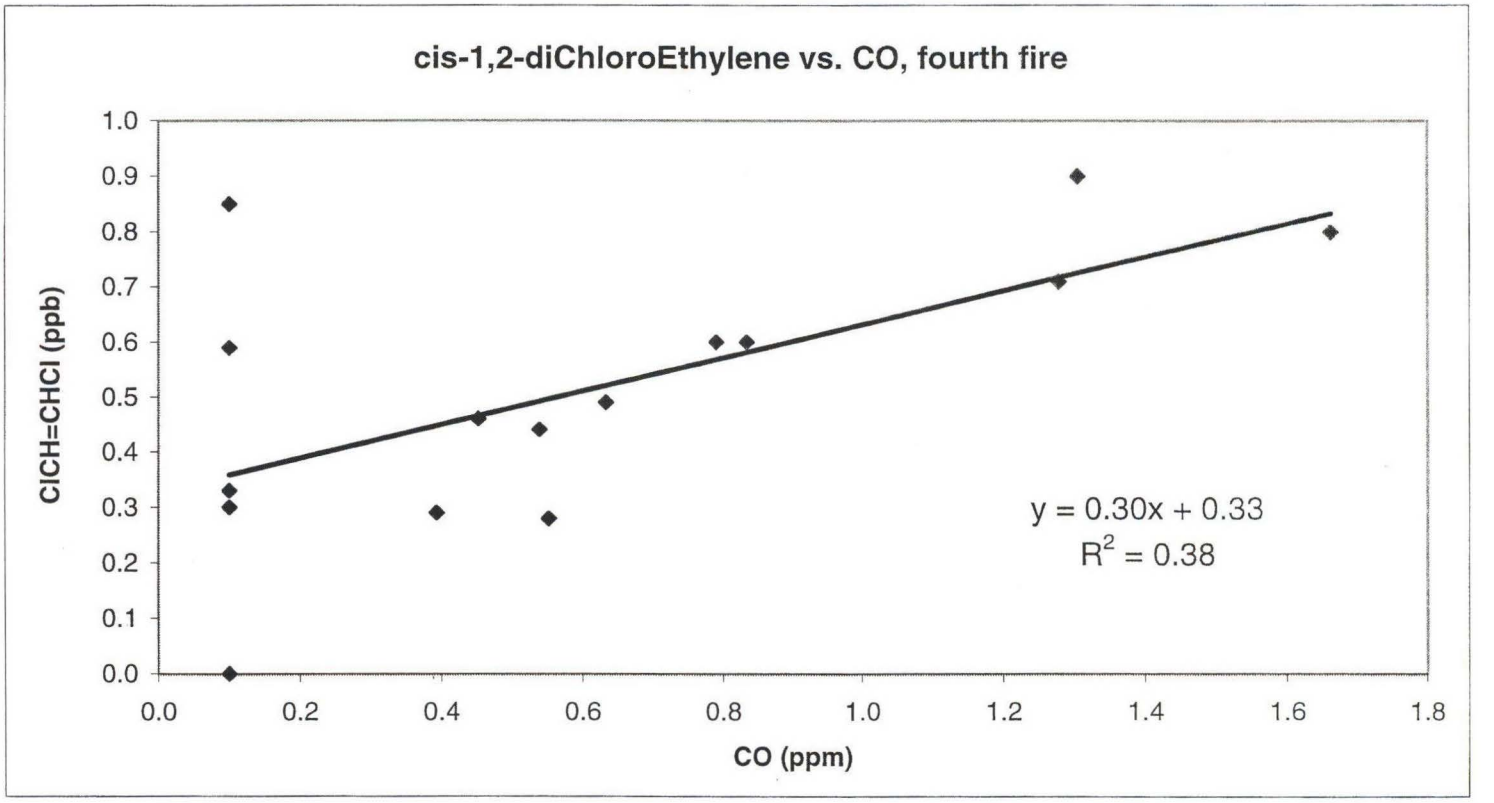
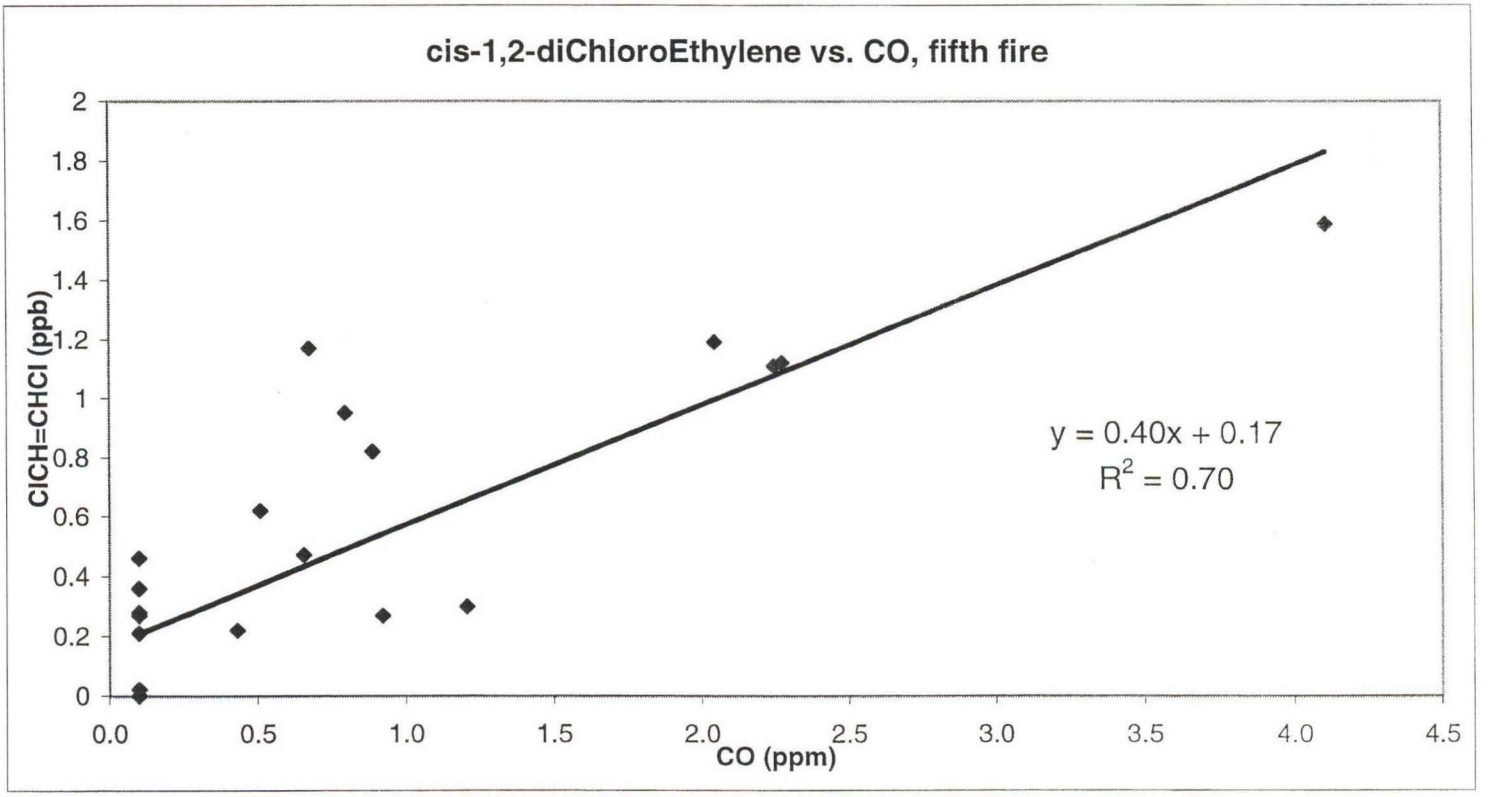


Figure 20. Alaska Fires. AirCraft Canisters.



VI. Conclusion

A method for trapping, concentrating, and measuring the halogenated hydrocarbon content of biomass burning emissions by gas chromatography was refined and utilized. Thirteen halocarbon gases were identified and quantified from the canister samples collected. The samples were from fires in diverse regions (Zambia, southeast U.S., and Alaska) and vegetation types (Miombo, Dambo, mixed forest and gallberry, and boreal forest). CFC's were measured at high levels in most of the samples but were all similar and showed no linear relationship with carbon monoxide (CO), a frequently measured gas that is a product of smoldering combustion. Six halogenated hydrocarbon compounds were found to have significant linear regression relationships with CO, at varying degrees for the fires sampled at the different sites. Of these the most important was methyl chloride, which was highly correlated with CO for most of the fires. Another compound which showed a strong linear relationship with CO for most of the fires was 1,1-dichloroethene. The CFC's were measured at high relatively constant concentrations for all samples, including background samples, indicating these compounds are not important components of biomass burning emissions. Methyl bromide was found at high at significant levels for some fires, indicating levels in emissions may be dependent on vegetation content.